

**Issues and Controversy:
The Measurement of
Crystalline Silica**

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Evaluation of the Detectability and Quantification of Respirable Crystalline Silica by X-ray Powder Diffraction Methods

by

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ABSTRACT

X-ray powder diffraction is one of the most sensitive methods for the analysis of crystalline forms of silica. In addition to detection and quantification, it can determine the specific crystalline species in the sample.

The principle limitations of the method depend on the effective volume of sample in the X-ray beam and the number of crystallites in the proper orientation to diffract. Detection limits are usually reported as 2 μ g in thin-film filter mounts and 0.1% in bulk samples that are free of interference from associated minerals. Filter methods are most often used for air quality monitoring and several standardized procedures have been certified. Standard procedures for bulk samples are difficult to certify because of the variability of the matrices and their potential interferences.

All the methods of quantification require calibration with known samples of quartz or cristobalite. Certification of standard samples involves characterization of the particle and crystallite size and size distribution and amorphous content as well as determining the X-ray diffraction response. Although quartz is readily available and cristobalite is easy to synthesize, preparation of quantities of sufficient uniformity and stability is a limiting factor in certifying such samples for reasonable costs.

Conventional diffraction equipment can be used for crystalline silica analysis at the present detection limits required by safety standards. Relatively simple modifications of the diffractometer will increase its sensitivity to small amounts of silica and improve the lower limits of quantification.

INTRODUCTION

Because of the potential health hazard of the crystalline forms of silica in the industrial environment, federal regulations require monitoring the presence of silica* forms in the workplace atmospheres and marketed products. From time-to-time, it is important to review and evaluate the regulations and methods for monitoring these crystalline silicas. This paper reviews and evaluates the use of X-ray powder diffraction for detecting, identifying and quantifying the crystalline and amorphous silicas in all types of samples from airborne dusts to bulk commercial products. This project has been sponsored by the Chemical Manufacturers Association.

Crystalline Silica in the Industrial Environment

The inhalation of dust as a primary cause of pulmonary disease has been a problem in the mining industry since antiquity. The problems were first termed pneumokoniosis by Zenker (1867), but the generic term has since been shortened to pneumoconiosis. The word originally implied that the lung had been seriously damaged by dust, but the meaning has been broadened to include all pulmonary manifestation of dust inhalation (Goldberg and Jacobson, 1972). The result of pneumoconiosis is to harden the linings of the lung by creating fibrous growths that make the lung effectively inoperative. Cures are impossible, so prevention is the goal of modern industry.

The most important form of pneumoconiosis is silicosis which could affect workers in many industries as well as in the mines. The cause of silicosis is primarily inhaled particles of crystalline silicon dioxide, SiO_2 , most commonly quartz which is a ubiquitous mineral in nature. The main technique for prevention of silicosis is to clean up the atmosphere that workers might inhale. Early prevention procedures in "hard rock" mining were to shift from drilling dry to drilling with water flushing the cuttings away from the working face. The freshly broken quartz particles from the quartz in the rocks and veins were extremely reactive both because of their angular shapes with active edges and because of the fresh surfaces. It is now known that ageing of quartz particles diminishes the activity but does not eliminate it, so it is necessary to reduce the atmosphere particulate content anywhere workers are liable to encounter crystalline silica.

* In this review the term "silica" will be used to imply a substance with the chemical composition SiO_2 or $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. "Crystalline" and "amorphous" will indicate the X-ray diffraction response to the material, where amorphous means no diffraction pattern is observed. The term "free" has no meaning when applied to crystalline silica and will not be used.

Modern practices in mines and industrial plants include directing the affected atmosphere away from the worker and into collector systems that remove the respirable particle component before the atmosphere is recirculated. The atmosphere and personnel

are continuously monitored by sampling devices that can accumulate the particulate matter in a quantitative fashion for subsequent laboratory analysis. These samples present the analytical laboratory with several challenges: the detection of the silica minerals in the sample, the quantification of the amount of crystalline silica in the sample, and the need to accomplish these measurements rapidly and accurately on large numbers of samples on a routine basis. Three methods are commonly employed: infra-red analysis, chemical analysis on treated samples and X-ray powder diffraction (Gebhardt, 1975 and Hamilton *et al.*, 1990). It is the purpose of this paper to review and evaluate the X-ray diffraction procedures in the light of modern equipment, sample handling and our understanding of the diffraction process.

Forms and sources of crystalline silica

Silicon dioxide, SiO_2 , may occur in many crystalline forms of which quartz is the most common. However there are many other polymorphs which may occur as natural minerals and/or are synthesized in the laboratory. Frondel (1962) presents a very comprehensive review of the mineralogy of SiO_2 discussing all mineral forms. Drees *et al.* (1989) reviews the occurrences of silica minerals in soils. Table 1 lists most of the known forms whose powder diffraction patterns have been recorded in the Powder Diffraction File (PDF, 1991). A few other clathrasils and some doubtful phases have been mentioned in the literature. Figure 1, redrawn from Ostrovsky (1967), shows the phase relations of the stable forms as a function of pressure and temperature. Only six forms appear on this diagram, and there is considerable question whether tridymite is truly stable. Achieving stability is always difficult in SiO_2 phase studies because of the sluggish nature of all the transitions. Once a major structure type is formed, it tends to continue to exist even outside its true stability field as a metastable phase. Figure 2, modified from Sosman (1955), shows diagrammatically the metastable behavior of the many polymorphs which can occur at atmospheric pressure. All of the major phases may be supercooled and superheated because of the sluggish nature of the transitions to the different structure types. Within each structure type, the transitions are fast because there are no bonds broken. The transitions are all caused by changing the angle of the Si-O-Si bonding as a function of temperature.

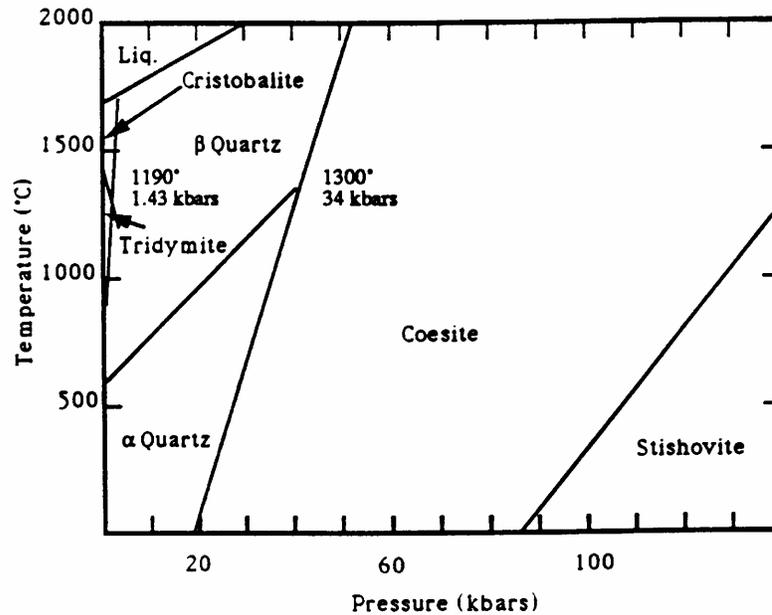


Figure 1. Pressure-temperature phase relations for SiO₂

Quartz Quartz is classified as a tetrahedral framework structure in which the Si is 4-coordinated to the O atoms which in turn bridge two Si tetrahedra to form a framework of tetrahedra with 6 and 12-membered loops. The bonding is estimated to be about 50% covalent and 50% ionic. There are two thermal polymorphs with the same framework topology; but the high-temperature form, stable above 573°C, is unquenchable, and only the low-temperature form is encountered in atmospheric samples or in the analytical laboratory. The composition shows very little deviation from stoichiometry; however, some water may be incorporated by breaking one Si-O-Si link with the formation of Si-OH HO-Si clusters. Quartz is considered to be chemically inert, reactive only in hydrofluoric and phosphoric acids and strongly basic solutions, but it does react in the lung linings to initiate fibrous tissue growth for unknown reasons. Whether the quartz acts as an irritant, a nucleation site, or is involved in the chemical reactions is not clear. By federal regulations, the permissible exposure limit, PEL, of quartz in the working atmosphere is 5% of the respirable particulates or 0.100 mg•m⁻³ during an 8 hour workday, and any product containing more than 0.1 weight percent quartz, cristobalite or tridymite must be labeled as a potential hazard.

Cristobalite Cristobalite is second most common crystalline form of SiO₂ which is encountered at ambient conditions. It is metastable at these conditions, but once formed persists indefinitely. It is also a tetrahedral framework structure composed of 6-membered rings. There are high- and low-temperature forms with the same topology, but as for quartz only the low form is encountered in industrial atmospheres. In spite of the shorter loops of tetrahedra, cristobalite has a more open structure than

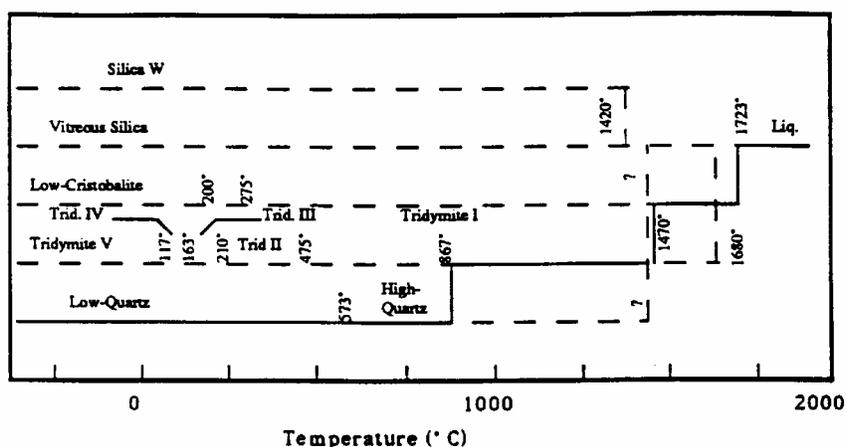


Figure 2. Metastability behavior of SiO₂ at ambient pressure.

Table 1. Crystalline forms of silica represented in the Powder Diffraction File.

Pattern #	Code Phase Designation	Cell Parameters (Å, degrees)		
PDF-46-1441	0M Lutecite [NR]	a = 8.77	b = 4.879 β = 90.08	c = 10.72
PDF-46-1242	0 (at 53 GPa)			
PDF-46-1045	* H Quartz	a = 4.91344		c = 5.40524
PDF-46- 570	CO	a = 5.01	b = 21.52	c = 11.13
PDF-45-1374	* T Stishovite	a = 4.1791		c = 2.6659
PDF-45- 131	CH Zeolite SSZ-24	a = 13.603		c = 8.277
PDF-45- 130	CH Zeolite SSZ-24	a = 13.671		c = 8.328
PDF-45- 112	* C	a = 24.225		
PDF-45- 111	i H	a = 17.17		c = 28.28
PDF-44-1394	CO + organic	a = 14.24	b = 20.14	c = 8.40
PDF-44- 696	i O	a = 20.05	b = 20.0	c = 13.4
PDF-43- 784	0			
PDF-43- 745	0			
PDF-43- 596	0			
PDF-42-1401	i O Tridymite	a = 17.0859	b = 9.9313	c = 16.3041
PDF-42- 22	CT	a = 20.067		c = 13.411
PDF-42- 5	i M	a = 9.91	b = 20.63 β = 99.7	c = 9.80
PDF-40-1498	*T	a = 10.2387		c = 34.3829
PDF-39-1425	*T Cristobalite, syn.	a = 4.9732		c = 6.9236
PDF-38- 651	iR Clathrasil	a = 13.887		c = 40.989
PDF-38- 360	M Moganite [NR]	a = 4.934	b = 10.761 β = 92.29	c = 8.533

PDF-38- 197	iO Zeolite O1	a = 13.836	b = 17.415	c = 5.042
PDF-35- 63	OO -----	a = 19.51	b = 13.98	c = 21.6
PDF-34-1382	0 Silica X			
PDF-34- 717	Silica X1			
PDF-32- 993	T -----	a = 12.75		c = 4.72
PDF-31-1234	0T Silica X2	a = 19.4		c = 14.50
PDF-31-1233	0T Silica Y	a = 15.50		c = 6.60
PDF-30-1127	0 -----			
PDF-29- 85	-----			
PDF-27- 605	iC Cristobalite, high	a = 7.13		
PDF-18-1170	iM Tridymite-1M	a = 18.504	b = 5.0064	c = 23.845
			$\beta = 105.84$	

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Codes

*, i, (blank), and 0 are PDF quality marks
C, H, R, T, O, and M indicate the crystal system.

Table 1(Cont.). Crystalline forms of silica represented in the Powder Diffraction File.

Pattern #	Code Phase Designation	Cell Parameters ($^\circ$, degrees)		
PDF-18-1169	H Tridymite, high	a = 5.046		c = 8.236
PDF-16- 380	0 -----			
PDF-16- 331	iC Melanophlogite	a = 13.402		
PDF-14- 654	M Coesite	a = 7.17	b = 12.38	c = 7.17
			$\beta = 120$	
PDF-14- 260	iH Tridymite-20H	a = 9.92		c = 81.5
PDF-13- 26	T Silica K (Keatite)	a = 7.46		c = 8.61
PDF-12- 708	H Quartz, disord.	a = 5.006		c = 5.459
PDF-11- 252	0H Quartz, high	a = 5.002		c = 5.454

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C, H, R, T, O, and M indicate the crystal system.

quartz, and traces of alkali ions may be incorporated in the cages combined with aluminum substituting for the silicon in the framework. Chemically, it is also considered inert with reactivity similar to quartz. With respect to silicosis reactivity, cristobalite appears more toxic than quartz, Wright (1978), but because it is less common than quartz, it has not received the attention in toxicology studies. The permissible exposure limit is set as one half the limit of quartz, *i.e.* $0.050 \text{ mg}\cdot\text{m}^{-3}$.

Other Polymorphs Other crystalline forms of SiO₂ include tridymite, coesite, stishovite, and melanophlogite which are natural minerals and keatite and several clathrasil-type forms which have no natural counterpart. Although all members of this list may be potentially toxic, only tridymite is listed as a hazardous material primarily because of its similarity to cristobalite in structure and chemical properties and its reported stability in the SiO₂ phase diagram. Wright (1978) states that tridymite has a similar toxicity to cristobalite and that stishovite seems to be unreactive. No evaluation of the other forms is given. The other minerals are very rarely encountered in nature or in industry. Tridymite is also very rare, and may actually not exist as pure SiO₂. All natural tridymite contains small amounts of Na, and it is impossible to synthesize without the presence of an alkali. Its structure is composed of tetrahedra linked in 6-membered loops similar to but with a different topology than cristobalite. The sluggish nature of the transition precludes its formation directly from quartz or cristobalite by heat treatment without the appropriate mineralizers present.

Opal Opal is a mineraloid of SiO₂•nH₂O which is paracrystalline to amorphous. It is a surprisingly common phase in nature, occurring principally in sedimentary environments. It forms as concentrations of siliceous animal skeletons such as diatoms and radiolaria which may form thick sedimentary layers. Opal also forms when ground water leaches silica from highly siliceous local rocks and soils and redeposits it as a silica gel in interstices and crevices. Opal also occurs in volcanic regions as a secondary reaction of hot water with the siliceous volcanic rocks.

Opal forms at low temperatures, typically less than 100°C, and is usually X-ray amorphous. As opal ages geologically, it dewateres and ultimately devitrifies to quartz as chalcedony, a cryptocrystalline variety of quartz. However, if the formation temperature is high, the opal may develop a structure very similar to cristobalite and/or tridymite. The effective crystallite size of this form is less than 500 Å, and its X-ray diffraction pattern is considered distinct from the truly crystalline forms of silica. On the basis of studies started by Jones *et al.* (1964), opal is classified into three forms: opal-A (X-ray amorphous), opal-C (resembles crystalline cristobalite), and opal-CT (shows a disordered form with some tridymite character).

Toxicity studies have been made only on the diatomite form of opal. Because of its amorphous nature, it is not easy to detect and quantify opal by X-ray diffraction. A diffraction pattern for opal-C has been reported which is listed in the Powder Diffraction File as PDF-38-448, and traces from opal-CT have also been reported in the literature. Heating amorphous opal to 1100°C will cause it to recrystallize as true cristobalite and allow its detection and quantification. However, other amorphous forms of silica also behave the same way. Table 2 lists all the hydrated forms of silica in the PDF. When monitoring for opal, it may prove necessary to monitor some of these forms as well.

Table 2. Crystalline forms of hydrated silica in the Powder Diffraction File.

Pattern #	Code Phase Designation	Cell Parameters (Å, degrees)		
PDF-46- 157	0 H ₂ Si ₁₄ O ₂₉ •xH ₂ O			
PDF-45- 423	0 H ₂ Si ₁₄ O ₂₉ •xH ₂ O			
PDF-38- 448	0 Opal, SiO ₂ •xH ₂ O			
PDF-37- 386	0 H ₂ Si ₂₀ O ₄₁ •xH ₂ O			
PDF-37- 385	0 H ₂ Si ₂₀ O ₄₁ •xH ₂ O			
PDF-35- 62	I T H ₄ Si ₈ O ₁₈ •H ₂ O	a = 13.80		c = 23.44
PDF-35- 61	0M H ₈ Si ₈ O ₂₀ •xH ₂ O	a = 8.14	b = 8.38 β = 94.0	c = 13.64
PDF-35- 60	0T H ₈ Si ₈ O ₂₀	a = 8.53		
	c=14.15			
PDF-32- 995	0 SiO ₂ •0.2H ₂ O			
PDF-32- 994	0 SiO ₂ •0.04H ₂ O			
PDF-31- 584	M H ₂ Si ₁₄ O ₂₉ •5.4H ₂ O	a = 7.11	b = 7.42 β = 94.0	c = 13.2
PDF-31- 583	0 H ₂ Si ₂ O ₅ •0.7H ₂ O			
PDF-31- 582	H ₂ Si ₂ O ₅ , beta			
PDF-31- 581	iM H ₂ Si ₂ O ₅ , beta	a = 11.287	b = 9.905 β = 103.78	c = 8.377
PDF-31- 580	H ₂ Si ₂ O ₅ , alpha			
PDF-31- 579	H ₂ Si ₃ O ₇ , alpha			
PDF-31- 578	H ₂ Si ₃ O ₇ , alpha			
PDF-29- 668	M H ₂ Si ₁₄ O ₂₉ •5.4H ₂ O	a = 7.11	b = 7.42 β = 94.0	c = 13.2
PDF-27- 606	O H ₂ Si ₂ O ₅	a = 7.47	b = 11.94	c = 4.91
PDF-25-1332	O Silhydrite, Si ₃ O ₆ •H ₂ O	a = 14.519	b = 18.30	c = 15.938
PDF-20-1051	T H ₂ Si ₆ O ₁₃	a = 13.000		c = 13.678
PDF-20-2049	0 H ₂ Si ₂ O ₅			

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*, i, (blank), and 0 are PDF quality marks

C, H, R, T, O, and M indicate the crystal system.

Occurrences of Silica Minerals Quartz is an extremely common mineral in nature. In fact, quartz is estimated to make up about 12% of the crust of the earth and up to 17% of the surface rocks. It is a common component of most soils and rocks. Some rocks such as beach sands and sandstones used for glass making, may be composed of more

than 95% quartz. There is probably no mining operation or industry employing natural materials that does not encounter quartz in the operations. In some industries such as ceramics, the quartz is essential to the products; but in mining, the goal is to separate the ore from the quartz so it may be discarded in the waste piles. The high concentration of quartz in soils affects the agriculture industry.

The occurrence of cristobalite in nature is quite rare. The phase diagram in Figure 1 shows that the effect of only a small amount of pressure is to cut out the cristobalite field in favor of high quartz. It forms in highly siliceous volcanic rocks that cool rapidly after extrusion. Such rocks, primarily obsidian, are rarely mined. Perlite, a related rock, always contains quartz as the silica phase. Cristobalite is also known to occur in sedimentary rocks as a devitrification product of opal or vitreous siliceous volcanic ash. This cristobalite may be used for foundry applications. Cristobalite is more common in industrial processes as the result of high-temperature processing of high-silica ceramics or as the direct devitrification product of vitreous silica or where crystalline silica is one of the product phases in a fired material. Tridymite occurrences in nature are reported to be the same as cristobalite but considerably more rare. Many reports of tridymite may actually be disordered cristobalite. Coesite and stishovite are only known from environments that have received shock pressures such as meteor impact sites. These other forms of silica are essentially unknown in industrial products.

Identification of the Crystalline Silica Forms The X-ray diffraction patterns of quartz and cristobalite are distinct from each other and from other minerals with which they may be associated, so X-ray diffraction methods are appropriate techniques for their detection, identification and quantification. Table 3 lists the diffraction patterns for the principal silica minerals, and Figure 3 shows the simulated diffraction patterns of these same minerals. The major peaks in the diffraction pattern for tridymite are distinct from cristobalite even though the structures have some similarity. The fact that tridymite has not been documented as a component of respirable silica has precluded the development of methods for its quantitative analysis, and the only methods in the literature are for quartz or cristobalite. Actually, it would be a simple matter to extend the present methods to tridymite by preparing suitable calibration curves and including the additional peaks in the diffraction studies.

Each of the principal minerals, except opal, has a few sufficiently strong diffraction peaks which may be used for quantification if other interferences are not present. The (101) peak of quartz is the best, but (100), (112) and (211) may also be used. The (101) peak for cristobalite is the best choice, and (211) is the best for tridymite to prove its presence even with potential cristobalite interference. Alternate peaks are available for both these phases.

Table 3. Low-angle diffraction patterns of the principal crystalline silica phases and opal

Quartz PDF-46-1045			Cristobalite PDF-39-1425			Tridymite PDF-18.1170			Opal PDF-38-448		
d	I	hkl	d	I	hkl	d	I	hkl	d	I	hkl
4.2550	18	100	4.040	100	101	4.328	90	040	4.08	100	
3.3435	100	101	3.515	<1	110	4.236	2	131	3.14	9	
2.4569	9	110	3.136	8	111	4.107	100	211	2.86	10	
2.2815	8	102	2.841	9	102	3.867	20	221	2.51	30	
2.2361	4	111	2.487	13	200	3.818	50	041	2.13	4	
2.1277	6	200	2.467	4	112	3.672	2	022	2.03	4	
1.9799	4	201	2.342	<1	201	3.642	4	112	1.937	5	
1.8180	13	112	2.1179	2	211	3.461	2	050	1.878	5	
1.8017	<1	003	2.0196	2	202	3.396	4	231			
1.6717	4	202	1.9294	4	113	3.250	4	150			
1.6592	2	103	1.8715	4	212	3.215	2	202			
1.6083	<1	210	1.7591	<1	220	3.017	4	311			
1.5419	9	211	1.7303	<1	004	2.975	25	042			
			1.6922	2	203	2.950	2	321			
			1.6349	<1	104	2.776	8	160			
			1.6122	3	301	2.609	2	023			
			1.6013	1	213	2.500	16	341			
						2.490	14	410			
						2.385	2	133			
						2.342	2	223			
						2.308	16	043			

Identification of the Amorphous Forms of Silica The direct identification of the several amorphous forms of silica is essentially impossible by X-ray diffraction unless the sample is a single homogeneous phase. There are undoubtedly several distinct structures for the amorphous states of silica. Silica glass is anhydrous and has a different type of tetrahedral linkage than is found in opal where the tetrahedra cluster into spherical agglomerates, and the water plays a role in the linkage. Other forms of amorphous silica may have different structures also as evidenced by the clathrasils formed from gel synthesis. The broad diffraction peak due to the structure of the particular state may shift in diffraction angle, but there is little else to distinguish the states.

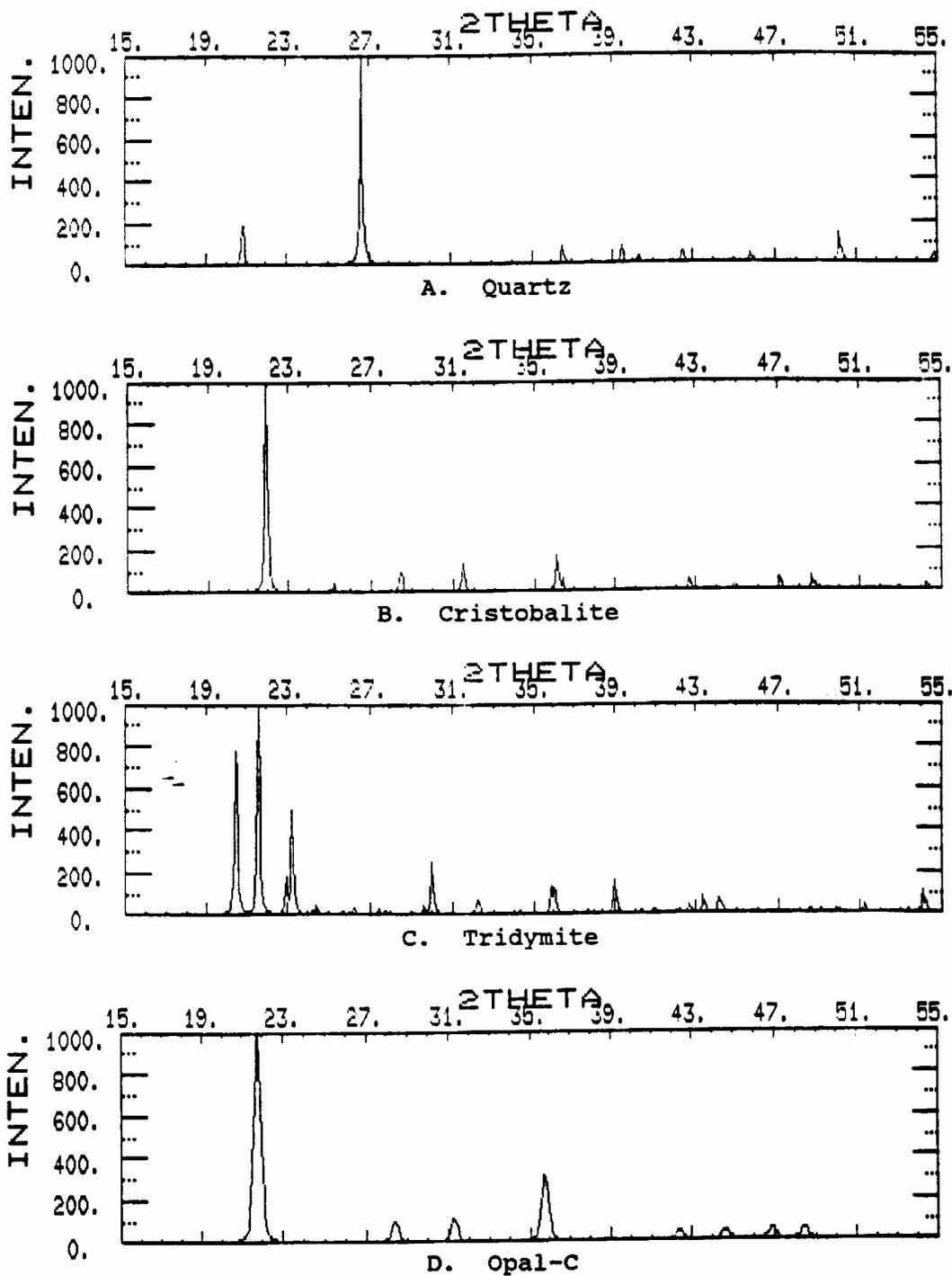


Figure 3. Diffraction patterns of the principal crystalline silica minerals. A. Quartz. B. Cristobalite. C. Tridymite. D. Opal-C.

Heating an amorphous silica usually causes it to recrystallize as cristobalite. Most samples will convert at temperatures as low as 1100°C, but further heating to

1450°C may be required to convert quantitatively the material. The thermal behavior of the sample would be more sensitive to the starting material than the final cristobalite. However, if the conversion is complete, the methods for quantifying cristobalite may be used to quantify the amorphous silica. Whether the conversion is affected by the presence of other phases in the sample needs to be studied.

Literature Review

There is considerable literature on the detection and quantification of the silica minerals by X-ray diffraction. An extensive review of all aspects of the silica problem was conducted by Babyak and Kamchak (1975, 1978), which contains many of the early references. The present list of references contain all of the papers published since 1948 that were located in a recent literature search. This date represents the real beginning of quantitative X-ray powder diffraction. No attempt was made to cover the large number of papers on quantification in general, although a few have been included among the references for specific purposes. Very detailed discussions of quantitative analysis may be found in Klug and Alexander (1974) and Brindley (1980). A very recent review of quantitative X-ray diffraction analysis published by Snyder and Bish (1989) covers most of the other pertinent literature. Recent reviews of silica determinations have been presented by Nenadic *et al.* (1971), Anderson (1975) and Hamilton *et al.* (1990).

The papers covered in this literature review may be classified as concentrating on laboratory procedures specifically for the determination of silica, evaluations of these procedures and inter-laboratory tests, analytical problems such as particle size and amorphous states, and discussions of theoretical and technical aspects of the quantification. These categories are indicated in the reference list.

Standardized Procedures As is necessary in any good routine type analysis, especially where the results may have legal implications, it is necessary to establish standard procedures for collecting and processing the samples. The procedures for the determination of respirable crystalline silica are primarily designed by governmental safety and health agencies to meet the requirements of federal health regulations. They may be modified by industrial analytical laboratories to meet specific needs and take advantage of local equipment. In the United States, the principal organizations are the Occupational Safety and Health Administration, OSHA, and the National Institute for Occupational Safety and Health, NIOSH. In the United Kingdom, it is the Health and Safety Executive, HSE; and in Canada, it is the Ministry of Labour. The procedures are listed in the reports section of the references. In addition to the reports, a few agency papers are in the open literature such as Abell *et al.* (1981b) and Anderson *et al.* (1976). Because of the importance of determining silica levels in mine atmospheres, the U. S. Bureau of Mines has also devoted considerable effort to silica analysis, and their reports are also listed.

Although the agencies have established the procedures, most of the analyses performed are done by service laboratories or by companies monitoring their own processes. Many of these companies have established their own procedures as dictated

by their needs, but the results are usually compared with test samples processed by both the developed procedure and the standard procedures. A review of silica procedures by Anderson (1975) has covered the earlier literature. Newer papers include Donovan *et al.* (1972), Allen *et al.* (1974), Altree-Williams (1977), Altree-Williams *et al.* (1977), Bumsted (1973), Davis and Johnson (1982a and b), Henslee and Guerra (1977), Machacek (19__), Malik and Viswanathan (19__), and Tossavainen (1979).

In addition to the procedures for determining quartz and cristobalite in respirable samples, there are several procedures for quantifying the levels of these minerals in bulk samples. These procedures are necessary because of the requirement that hazard labels be applied to any product that contains 0.1 weight percent crystalline silica. The more recent papers include silica analysis in clays (Murray and Merkl, 19__; Carter *et al.*, 1987); paint (Kamarzchik, 1980); coal, (Davis *et al.*, 1986); dolostone (Emig and Smith, 1989); and rocks (Pawlowski, 1985). A general review of the theory and methods used for bulk analyses is presented by Snyder and Bish (1989).

Evaluations of Standard Procedures In order to establish confidence in the use of standard procedures, it is necessary to test the methods in the working laboratories. Several tests are described in the literature. Several of the tests were monitored by NIOSH personnel or contractors including Peters (1976), IIT (1983), Giles and Cee (19__), and A. D. Little, Inc. (1976). Other reports appear in the open literature including Donovan *et al.* (1972), Edwards *et al.* (1955), Chung (1982), Nagelschmidt (1956), and Pickard *et al.* (1985). All these tests indicate that reproducibility and accuracy of the results were not within the desirable tolerance limits, which is why there has been so much effort applied to improving the analysis methods.

PRINCIPLES AND PRACTICES OF QXRPD

Basic Theory and its Significance in Silica Determinations

Fundamental Equations The fundamental equations of quantitative X-ray powder diffraction analysis were first formulated by Alexander and Klug (1948). For a phase J in a mixture, there is an equation for the intensity of each *i*th diffraction peak with the form

$$I_{ij} = \frac{K_{ij} x_J}{\rho_J \mu^* M} \quad (1)$$

where x_J is the weight fraction of phase J, ρ_J is the density of phase J, K_{ij} is the intensity constant for peak *i*, and $\mu^* M$ is the mass absorption coefficient for the mixture. K_{ij} may be determined from the pure sample by

$$I_{ij}^0 = \frac{K_{ij}}{\rho_J \mu^*_{iJ}} = \frac{K_{ij}}{\mu_J} \quad (2)$$

where μ^*_{iJ} and μ_J are the mass and linear absorption coefficient respectively for phase J, both of which may be found in tables. If the absorption coefficient can be measured for the mixture, equation 1 may be solved for the weight fraction of J.

Where the sample is not infinitely thick, the expression contains an additional term:

$$I_{ij} = \frac{x_J K_{ij}}{\rho_J \mu^*_{iJ}} (1 - e^{-2\mu_J M \cos \theta_{ij}}) \quad (3)$$

M is the weight per unit area of the sample, and θ_{ij} is the Bragg angle of the diffraction peak. Expressions 1 - 3 are known as the direct method or absorption correction method. The diffraction experiment is setup to allow the measurement of both the peak intensity and to determine the effective mass absorption coefficient by experiment. Use of the absorption method is discussed by Leroux *et al.* (1953), Williams (1959) and Davis and Johnson (1987).

The Internal Standard Method Because of the complications of measuring the absorption coefficient in most cases, especially in very thin samples, other methods have been devised. If one adds a known, fixed amount of a reference phase to every mixture, the ratio of analyte to standard is a linear function of the weight fraction of the analyte through the relation:

$$x_J = k'_{JS} \frac{I_{ij}}{I_{kS}} \quad (4)$$

where I_{kS} is the intensity of a specified peak of the added reference material and k' is a constant that may be determined by calibration with known mixtures. This approach is known as the "internal standard method." It has been further formulated by Chung (1974a) as the "adiabatic" method. Although this method has been used for respirable dust analysis, it is not practical for silica analysis using membrane filters because of the difficulty of adding the standard. The internal standard method has the advantage that individual phases of the mixture may be analyzed independently of all the other phases in the mixture. Examples of the use of an internal standard in silica determinations are given by Gordon *et al.* (1952), Griffen (1955), Talvatie and Brewer (1962) Kupka (1967), Orberg (1968), Bumsted (1973), Aintree-Williams *et al.* (1977) and others.

The External Standard Method Another method is called the "external standard method" which is also known as the "reference intensity method" by Davis (1986) or the "matrix flushing method" by Chung (1975). It is most simply expressed as

$$\frac{x_I}{x_J} = K \frac{I_{iI}}{I_{jJ}} \quad (5)$$

where x_I and x_J are the weight fractions of phases I and J respectively and I_{iI} and I_{jJ} are the intensities of selected peaks in the diffraction pattern. The calibration constant K can be determined in a 1:1 mixture of I and J where $x_I/x_J=1$ as

$$K = \frac{I_{jJ}}{I_{iI}}. \quad (6)$$

K values may be determined against any reference material S (commonly α -alumina, corundum) using 1:1 mixtures then

$$K_{IJ} = \frac{I_{jJ}/I_{kS}}{I_{iI}/I_{kS}} = \frac{K_J}{K_I}. \quad (7)$$

If the weight ratio of every phase in the mixture is determined and the mixture is totally crystalline, then the relation

$$\sum_{k=1}^N x_k = 1 \quad (8)$$

allows the individual weight fractions to be determined. Sometimes this method is referred to as "quantitative analysis without standards", but the standards are external. Karlak and Burnett (1966) were the first to formulate this approach which was followed up by Chung (1974b and 1975). Many authors have discussed this method and the measurement of the reference intensity values for many materials. Hubbard *et al.* (1976) evaluate the use of these RIR values for quantitative analysis. Davis (1984, 1986b and 1988), Hubbard and Snyder (1988) and Snyder (1991) further discuss the RIR method of analysis.

In recent years, the term "standardless" quantitative analysis has appeared in the literature for an extension of the external-standard method. When there are many samples with the same phases, all the diffraction data may be collected first, then the full set of equations may be solved simultaneously. Usually, additional physical or chemical constraint equations are included in the set of equations. The sum of the weight fractions of all the phases being equal to unity is one example of a physical constraint. The term was first introduced by Zevin (1977), and the approach has been further developed by

Zevin and Zevin (1983), Rius (1987), Wang (1988) and Wang *et al.* (1991). This approach is not useful for the determination of silica because it does not establish a procedure to process many samples where only one phase is being quantified.

Determination of the appropriate reference-intensity ratios, RIR, is best done by experiment on the same equipment and with the same sample preparation technique as is being used for the analysis, but sometimes appropriate samples are impossible to acquire or synthesize. The alternative approach is to use calculated diffraction data to generate a RIR value based on known crystal structures. The most common program for this purpose is POWD12 (Smith *et al.*, 1982). Discussions on the use of calculated references data are given by Hubbard *et al.* (1976), Hubbard and Smith (1977), Atree-Williams (1977), Goehner (1982) and Smith *et al.* (1988). These calculated RIR values are for infinitely thick samples. Appropriate changes must be made when they are to be used for thin samples. This problem is discussed by Davis (1984).

Intensity Scales The magnitude of the measured intensities depend on several factors: the scattering power, K_{ij} , of the compound in the sample and the amount present, x_j ; the strength of the incident X-ray beam; the count time selected for the measurement; and the efficiency of the detection system. Consequently, the intensities must be placed on some common scale for interpretation. There are three scales which are used in diffraction studies: the relative scale, the relative-absolute scale and the absolute scale. The relative scale normalizes the strongest peak to 100 and lists all the other peaks proportionately lower. This scale is useful for identification. The relative-absolute scale may be achieved by referencing measurements to some standard, the reference intensity method. This method is the most common method used in bulk quantitative analysis, and its basis was first described by Visser and deWolff, (1964). The absolute scale would involve all the factors in the expanded intensity equation to place the intensity on a scale in terms of intensity units. This scale is only used in very specialized diffraction experiments and requires very elaborate instrumental calibrations.

Advantages of QXRPD for crystalline silica

Sensitivity of XRD to Specific Phases The basic principle of quantification with X-ray diffraction is that the measured intensity is proportional to the amount of the phase in the mixture modified by the effect of absorption as seen in equation 1. The diffraction effect is dependent on the nature of the crystalline structure of the phase resulting in diffraction patterns which are usually distinctive as is the case for the silica polymorphs. It is apparent in Figure 3 that the particular polymorph may be easily identified, which is impossible from chemical information alone and difficult from other spectroscopic measurements.

The principal source for diffraction pattern information that distinguishes the different phases is the Powder Diffraction File using the data in Table 3 which have been reported in the PDF (1991). If the form of silica is not known, the procedure would be to collect a fast scan diffraction pattern and then to match the d's and I's from the pattern with the data for these phases or other phases in the PDF. Although the probability that a

different form of silica will be encountered other than quartz or cristobalite is small, the possibility exists, and XRD is the only method to provide positive identification. Also, the other forms of silica may be toxic, so it is necessary to have the ability to confirm the presence of the other forms. If any of the other forms are encountered in any significant quantities, then it will be necessary to establish a quantification procedure for its determination.

Interferences in XRD Both quartz and cristobalite have relatively few diffraction peaks in their patterns as shown in Figure 3, and quantification of these phases is usually little affected by minor amounts of other phases. However, atmospheric samples and most bulk product samples usually do have interfering phases present. Atmospheric samples, especially those from mines, may contain other "predictable" minerals. Some of the minerals do not cause problems, such as calcite and dolomite (Emig and Smith, 1989), but micas and clay minerals which often accompany quartz do interfere. Knight and Zawadski (1989) discuss some interferences in mining environments. If the interference only affects the strongest of the analyte peaks, the alternate peaks may be used with a concomitant decrease in detectability and accuracy due to the weaker intensities employed.

Table 4, modified from Pickard *et al.* (1985) and HSE/MDHS 5 1/2 (1988), lists some of the interferences from common "impurity" minerals. This list pertains specifically to atmospheric samples but could apply to other situations. Most of the minerals overlap with the strongest quartz peak, (101), requiring an alternate choice of quartz peaks or a rather unsatisfactory correction of the (101) intensity by estimating the amount of the interfering phase and subtracting its contribution to the quantification peak. For phases such as aragonite and kaolinite, there is no option because all the quartz quantification peaks are overlapped. The alternative approach when overlap is severe is the whole-pattern fitting procedures discussed elsewhere in this review.

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Table 4. Potential mineral interferences with quartz. Modified after MDHS 5 1/2 (1988) and Pickard et al. (1985).

Quartz quantification peak	(100)	(101)	(112)	(211)
Relative intensity	22	100	14	9
Diffraction angle	20.86	26.66	50.18	59.98
Mineral				
Albite	-	+	+	+
Anorthite	+	+	-	-
Aragonite	+	x	+	+
Barite	-	x	x	-
Biotite	-	x	-	+
Cristobalite	-	-	-	+
Graphite	-	x	-	+

Kaolinite	+	-	+	+
Maghemite	+	+	+	-
Microcline	+	+	-	-
Mullite	-	x	-	+
Muscovite	-	x	-	-
Sillimanite	-	x	+	+
Tridymite	x	+	+	+
Wollastonite	-	+	+	+
Wustite	-	-	-	x
Zircon	-	x	-	+

=

- no interference
- + minor interference
- x major interference

Automation of the Analysis Procedure There are two primary reasons to automate sample processing, but the dominant one is because of the large number of samples which usually must be processed. The other reason is the intensive but routine calculations which are involved in the reduction of the data. A third reason is to maintain the sanity of the operator. With the increased use of computer-controlled APD's, automation is realistic and relatively easily achieved. Sample automation requires a sample changer on the diffractometer which is usually available for all APD's in use. The control of the sample changer is in the software of the APD. If every sample is processed in a preset manner, the APD software usually is adequate for data collection. However, if the diffractionist wants to interrogate the data, such as testing the main peak to set the count time for subsequent integrations, software patches may be required. Once the intensity data are obtained, the data may be transferred to a data reduction package for producing the quantification values. This software may be part of the APD package, but more often it will have to be supplied by the user. Examples of automation for silica analyses is presented by Bumsted (19__), Abell *et al.* (1978), Malik and Viswanathan (19__), Snyder *et al.* (1981, 1982 and 1984), Hubbard *et al.* (1983) and Wong *et al.* (1983).

Non-Destructive Nature of X-ray Diffraction One important and often-quoted advantage of XRD methods is the non-destructive aspect of the treatment of the samples used in the analysis. Other than the need to crush some samples, no other change is induced in the samples by the X-ray experiment. This aspect is particularly useful in silica analyses where alternative procedures may be run in parallel with the X-ray analysis. Also, the sample may be retained for later measurement which is especially valuable in situations involving legal disputes.

One problem, which will be discussed in more detail later, is the controversy whether the collection membrane filter may be used directly in the diffractometer or whether the dust must be reprocessed to achieve the desired accuracy. Because the sample may be saved, the direct method may be used first, and then the more time-

consuming method may be employed if there is any reason to doubt the results. Fortunately, membrane filters do not require much space for storage, and the silica phases are stable over time, but the handling must be done carefully so as not to lose any of the dust particles at any step.

Crystallite versus Particle Size Throughout the discussions of particulate behavior in X-ray diffraction samples and experiments, there is a need to carefully distinguish between particle size and crystallite size. Particle size is the size of the discrete particle which is the entity that is important in interpreting absorption effects. The crystallite size is the size of the effective crystal domain which contributes coherently to the diffraction experiment. This size contributes to peak broadening and is the entity to be considered in the discussions of crystallite orientation and intensity response for a sample. In many cases the particle size and crystallite size are synonymous. Where a quartz crystal is crushed to prepare a reference sample, the fragments are individual crystallites. Crushing of polycrystalline products may lead to single-crystal particles also, but not necessarily. The diffractionist must remember these distinctions. Although particles will be considered individual crystallites in the discussions that follow, the distinction will be kept clear where the distinction could be important.

Problems of QXRPD

Orientation and Crystallite Statistics X-ray diffraction techniques are not without their problems. There are two very severe sample problems which must always be considered (crystallite orientation and crystallite statistics) and several less severe problems (extinction, detector response, and microabsorption) which must be considered. The orientation problem is whether the crystal domains that make up the sample are randomly oriented in space which is the basic assumption on which the powder method is based. Accurate quantification is impossible if this condition is not met. The statistics question is concerned with whether the effective number of crystallites in diffracting position is sufficiently large to satisfy the statistics of sample representation. The statistics problem has been considered by Alexander *et al.* (1948), deWolff (1958) and deWolff *et al.* (1959). Because of the critical nature of these problems, a detailed discussion of the analysis of orientation and crystallite statistics is included in later section. The result of this analysis is to show how critical the crystallite size and the number of crystallites in a sample may be to the potential accuracy of the diffraction experiment.

The crystallite analysis is directly attributable to the bulk sample which has infinite thickness, but the principles also apply to the thin-layer sample. If the sample is assumed to be one crystallite thick, all the crystallites in the sample may contribute to the diffracted intensity. The effective number of crystallites in the proper orientation to diffract in a thin-layer sample may be estimated from the total number of particles as is done for the bulk sample. If the average particle size of the respirable dust sample is 2 μm , and if the total weight of the sample is 2 mg, there are 1.8×10^8 particles in the sample and 3860 in a position to diffract assuming true randomness. Assuming all the

particles are quartz, the predicted absolute accuracy is of the order of 4 %. Smaller quantities of quartz will be proportionately less accurately determined. The orientation and crystallite statistics are the most important property of the sample in defining the accuracy of the QXRPD method.

Extinction Extinction effects in crystals may be divided into two categories: primary extinction where the crystal is perfect and causes multiple diffraction within the crystallite and secondary extinction where the crystal is "ideally imperfect" and aligned domains cause the multiple diffraction. Both effects diminish the strength of the diffracted beam compared to what it should have been without the effect and affect the stronger intensities proportionately more than the weaker intensities. Cline and Snyder (1987) have discussed the seriousness of this effect. The order of magnitude of the problem may be illustrated by considering the PDF data for quartz. PDF-33-1161 shows that the intensity for the (100) quartz peak was measured as 22 on the scale of (101) normalized to 100. The POWD12 (Smith et al. 1982) calculated diffraction pattern for quartz shows the theoretical intensity for (100) should be 17. The experimental ratio indicates that around 25% of the intensity of the strong peak was lost to extinction. The usual perfection of quartz crystals used for preparing such standards suggests that primary extinction is the cause. The particle sizes for the PDF pattern were not reported, but it is probable that the average was not less than 10 μm . Smaller crystallites show less extinction, but even submicron particles will not be free of the problem. If the perfection of the crystallites can be destroyed by some treatment (such as radiation damage), the effect can be minimized. As long as the reference material used for preparing calibration curves has the same perfection as the samples to be analyzed and the particle size distribution is equivalent, the results will be acceptable.

Detector Response Modern scintillation and solid-state detectors can handle relatively high counting rates in the diffracted beams, but for quartz, which is a very strong diffractor, departure from linear response might occur on the (101) peak when the amount of quartz is high. Usually, the departure is negligible if the counting rates are below 1×10^4 counts/sec. At higher count rates the diffractionist should consider this potential error. An example of the effect of deadtime in counting is the comparison of the now deleted PDF-5-490 to the active PDF-33-1161. In PDF-5-490 the intensity for (100) is 35. The more recent measurements show (100) with an intensity of 22. The old diffraction pattern was taken with a Geiger-Mueller counter with a long deadtime. The effect was to diminish the intensity of the (101) peak by over 35%. This intensity difference is not trivial.

Microabsorption Large particles with different absorption magnitudes cause particle masking known as microabsorption. This effect has been analyzed by Brindley (1945) who derived correction formulae when the particle sizes were in excess of 1 μm . A detailed discussion of the effects of microabsorption on quantitative analysis was presented by Cline and Snyder (1987).

The Integration of Diffraction Peaks by Profile Fitting

When using the individual peak approach for quantifying one or more phases, all is not lost if there is overlap with peaks of other phases. If the raw data is a digitized trace including the peaks of interest and the peaks which interfere, modern profile fitting may be used to decompose the clusters into individual profiles thus determining the individual peak areas.

Profile fitting was first proposed by Rietveld (1969) where it was coupled with a refinement of the lattice parameters and the crystal structures. Many authors have extended Rietveld analysis to be more versatile and to be usable for quantitative analysis as mentioned in another section. Alternatively, there have been several programs developed which decompose peak clusters into individual component profiles without any constraints or with only constraints imposed by fitting peak positions to be compatible with a specific unit cell. Howard and Snyder (1982) have discussed procedures to be followed in profile fitting. Schreiner and Jenkins (1982) discuss profile parameters such as width and shape to be considered when fitting. The basic concept is to use a single resolved peak of a phase to fix the profile shape parameters before fitting other peaks of the same phase. An example of profile fitting for quantitative applications is given by Werner *et al.* (1979).

Major problems occur when the sample is a multiphase mixture with some phases having broad profiles while others have sharp profiles. In this situation, each peak must be fitted without restraining the parameters which can lead to incorrect results. The Appendix contains a list of programs for profile fitting. Proper use of an appropriate program can yield good integrated intensities for quantitative analysis.

SAMPLES AND SAMPLING

The Nature of Samples for X-ray Diffraction Analysis

Bulk Samples Samples used in crystalline silica analyses are usually of two types. One type of sample is the small block or cut section from a large block, and the other is a crushed sample. A bulk sample is defined as one whose thickness is sufficient so that no further increase adds to the intensity of the measured diffracted beam. This thickness is termed the "infinite" thickness, and is related to the linear absorption coefficient by the relation

$$t_{\infty} = 3.2 \frac{1}{\mu_M} \frac{\rho}{\rho'} \sin\theta, \quad (9)$$

where ρ and ρ' are the particle density and the sample density including void space respectively. For a sample dominated by quartz with $\rho = 2.65 \text{ g}\cdot\text{cm}^{-3}$ and $\mu = 91.3 \text{ cm}^{-1}$, this thickness is around 0.33 mm. This thickness would require about 0.2 g of sample for a typical diffractometer. This amount is two orders of magnitude larger than the typical filter sample.

Bulk samples are employed where the question is the level of crystalline silica in a product. Usually, there is little difficulty obtaining sufficient sample for the analysis, and the sample can reasonably represent the product if the sampling procedure followed good statistical practices. As will be discussed below, the most common problems encountered quantifying bulk samples are reducing the particle size to the $<5 \mu\text{m}$ range and preparing the particles in a truly randomly oriented manner.

The preparation of bulk samples is an art that is not easy to master. Hutchinson (1974), Smith and Barrett (1979), Jenkins *et al.* (1986), Bish and Reynolds (1989) and Miola and Ramani (1991) have reviewed sample preparation techniques in considerable detail. The biggest single problem is preferred orientation of the crystallites in the sample. Calvert *et al.* (1982) have tested the many methods proposed to eliminate orientation by comparing the results with a sample of MoO_3 , a very difficult material to prepare in a random mount. Side drifting and spheroidizing are the most successful. Smith and Snyder (1979a and b) have developed the spray-drying technique specifically for X-ray diffraction. If there is sufficient sample, usually several grams, then the spheroidizing approach may be employed.

Bulk samples require absorption corrections or the use of one of the reference methods. All the theory is derived for the infinitely thick sample, and a thinner sample presents additional correction problems. Calibrations based on an intensity response for quartz compositions in standard samples would have to be applied carefully. If the matrix absorption effects are matched, the standard curve can apply. The measurement of the effective absorption value for each sample has been used to correct such calibration curves with some success, but such corrections usually reduce the accuracy because of the additional measurements involved. Because of the size of bulk samples, it is usually convenient to add an internal standard and use appropriate calibration curves or to use the external standard method.

Thin Samples The second type of sample is the thin sample which is ideal if the layer is closely packed and one grain thick such that no single grain masks any other grain. This type of sample is prepared by drawing a fluid suspension of particles (either air or liquid) through a porous membrane filter. The filter is usually an organic film so it does not contribute significant to the diffraction, but silver is also used where a diffraction effect is desirable.

Techniques for preparing thin samples on filter substrates have been developed since the early 1950's. They have been used extensively in the analysis of clay minerals where samples are prepared to deliberately orient the clay particles, and that literature should be consulted (Bish and Reynolds, 1989). Kupel *et al.* (1968), Leroux and Powers (1969), and Bumsted (1973) developed techniques specifically for respirable quartz which has been improved by Atree-Williams (1977), Kolk (1985), Kohyama (1985). Pollack (1975), Davis and Johnson (1982a), Lippman (1983) and Davis (1986) have expanded the technique to prepare filters from small to bulk samples not collected in an personal sampler. Carsey (1987) has devised a larger chamber system, LISA, to evaluate

sampling techniques and samplers. Bartley and Doemeny (1986) have discussed sampling procedures.

The thin sample does not require an absorption correction because no particle masks any other particle. Thus, the intensity response is linear with respect to the amount present on the filter within the area of the filter irradiated by the incident X-ray beam. Calibration curves may be prepared by distributing known or measurable weights of silica on the filter and measuring the integrated intensities of the peaks. Even the presence of highly absorbing additional particles will not affect the linearity of the response because there are no masking effects.

Where the deposits are made on silver filters, it has been shown that even in thin samples, some of the particles are drawn into the pores of the filters. These particles are partially masked from the X-ray beam by the surrounding silver and cause the intensity response to depart significantly from linearity. If the loading of the sample is too heavy, greater than 2 mg, then particles will deposit on top of each other thus masking the hidden grains. For such a sample, a matrix correction is necessary as indicated in equations 1-3 which can be obtained by measuring the attenuation of the intensity of a peak from the substrate if it is crystalline such as silver. It is preferable in the filter method to avoid the need for the absorption correction if possible because the correction is not very accurate for a 2 to 3 mg layered sample.

Because of the small number of particles in the filter sample, it is difficult to add an internal standard for sample calibration purposes. CaF_2 has been used by Orberg (1968) and Bumsted (1973) and others. MgO , NiO and other compounds have also been used. The use of reference intensity methods is also difficult because the values reported in the literature apply to bulk samples not to thin samples, and appropriate values would have to be measured. Obtaining appropriate RIR values for thin samples of quartz would require depositing thin, single-grain layer samples of mixtures of quartz and a standard. As is discussed in the section on statistics, there are insufficient particles to yield much accuracy to the RIR values measured in this manner.

Also, because of the small size of the thin-layer sample, there is always concern as to how representative the particles are of the sample that was tested. In the case of dust analyses, the sample is not just the particles collected, but the volume of air sampled. Thus, the accuracy of the measurement is limited by the number of particles as discussed in the section on crystallite statistics.

Crystallite Statistics

This section is taken from Smith (1992). Regardless of the technique employed, the conditions for accuracy, which are very sample dependent, are the same--total randomness of the crystallite orientations, sufficient crystallites in the experimental sample to meet statistical requirements and sufficient intensity measured to meet counting statistics. Randomness may be described by selecting an equivalent general direction in all crystallites and examining the distribution of this direction vector in space

for all the crystallites in the sample. "Particle statistics" requires determining how many of these crystallites will diffract in the experiment and whether they are sufficient to allow intensity measurements to the desired accuracy. These conditions will be examined in more detail.

The conditions of randomness may be described by circumscribing a sphere of unit radius about the sample and plotting the intersection of the poles (direction vector or diffraction vector if the pole is perpendicular to the Bragg plane) on the surface of the sphere. Because the direction selected was general, every direction in the crystallites should behave similarly. Randomness requires the pole density (number per unit area) to be uniform over the surface of the sphere. Randomness may be achieved with any number of poles (crystallites in the sample) as shown in Figure 4. When the number of poles is small, the angle between adjacent poles is large, so that only a few grains in the sample can meet the conditions for diffraction. The average angle between poles is

$$\alpha_p = \sin^{-1}(4/\sqrt{\pi\eta}) \quad (10)$$

where η is the number of crystallites in the sample.

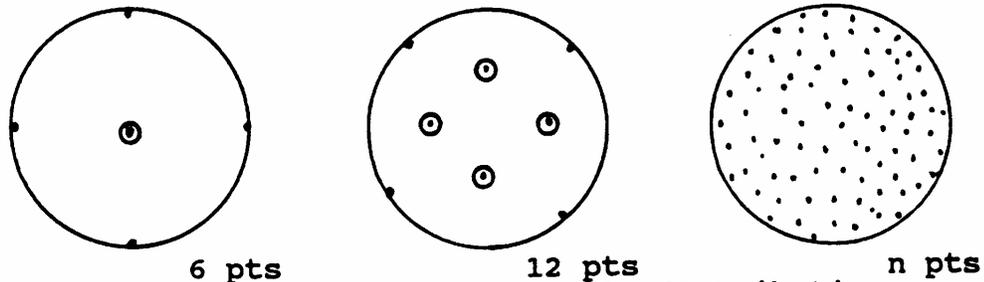


Figure 4. Stereograms of random pole distributions

The number of crystallites in a sample depends on the volume irradiated by the X-ray beam and the crystallite size. Assume the irradiated area is 1 cm^2 . The volume of the sample depends on the depth of penetration of the beam. A good estimate of the effective depth is twice the half-depth of penetration

$$t_2 = \frac{1}{\mu} \quad (11)$$

For SiO_2 and $\text{CuK}\alpha$, $\mu = 97.6 \text{ cm}^{-1}$ which is approximately 100 cm^{-1} . Thus, the effective volume is essentially 20 mm^3 . The crystallite size in the sample depends on how the sample was prepared. If the sample was crushed and sieved, the maximum particle size will be determined by the screen size as shown in Table 5. Because the 400 mesh screen is a commonly used size, $40 \text{ }\mu\text{m}$ crystallites are generally thought to be sufficiently small for accurate quantification. The effect of this size will be compared to $10 \text{ }\mu\text{m}$ and $1 \text{ }\mu\text{m}$ sizes in the discussion which follows. Crystallite size will also be considered equal to particle size.

Table 5. Screen mesh and particle sizes

Screen Mesh	Effective Particle Size (μm)
200	74
325	47
400	38
600	25
1000	10

Table 6 compares the particle populations in a sample. There are less than a million crystallites in the 40 μm sample compared to over thirty billion in the 1 μm sample. The low population of the 40 μm crystallites yields an average angle between the poles of 10 minutes of angle compared to 2.5 seconds in the 1 μm sample. This difference has a significant effect under the diffraction conditions of a sample.

Table 6. Particle Size Comparisons

Diameter	40 μm	10 μm	1 μm
Volume per crystallite	3.35×10^{-5}	5.24×10^{-7}	5.24×10^{-10}
Crystallites per 20 mm^3	5.97×10^5	3.82×10^7	3.82×10^{10}

Figure 5a shows a sample irradiated with a beam of radial divergence angle γ . The divergence angle is much wider than any of the crystallites in the sample, so it is not this divergence angle which defines the diffraction conditions of any individual crystallite. As shown in Figure 5b, it is the size of the X-ray source which limits the angular range over which a single grain may diffract. Although different crystallites within the sample (see Figure 3a) may diffract within the divergence angle γ , each crystallite is limited to the range α_s where

$$\alpha_s = \sin^{-1}\left(\frac{F + d_s}{R}\right) + \beta_s. \quad (12)$$

Where F is the apparent width of the X-ray source, d_s is the diameter of the crystallite, R is the radius of the diffractometer, and β_s is the rocking angle of a crystallite. The rocking angle of a crystallite such as quartz is of the order of 15 seconds (0.0042°). Thus, β_s for a typical fine-focus diffraction source and $40 \text{ }\mu\text{m}$ crystallites is around 0.044° , about 1/4 of the average angle between the direction vectors of the crystallites. It is quite apparent that a $40 \text{ }\mu\text{m}$ crystallite size will have too few crystallites to meet the diffraction conditions necessary for statistical significance of the intensity measurements.

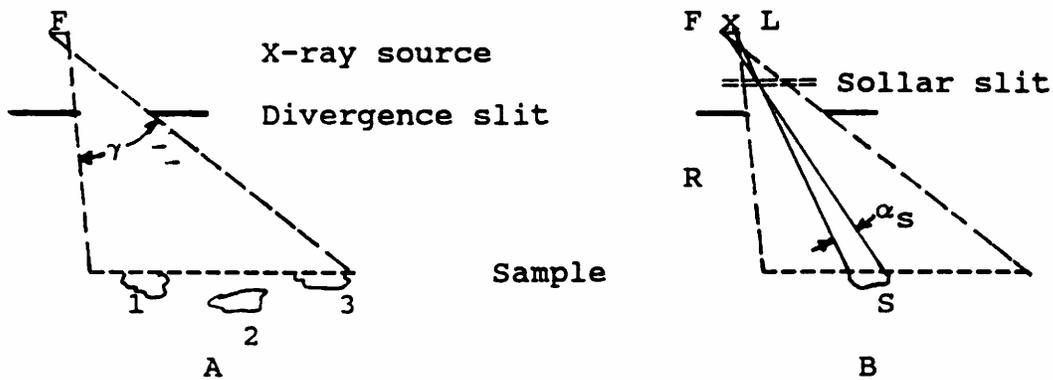


Figure 5. A. Diffractometer optics for incident rays. B. Effective ray paths for a single crystallite.

To analyze fully the number of crystallites in diffraction in a particular sample, axial divergence effects also need to be considered. The length of the X-ray source also limits the angular range in the axial direction. This length depends on the soller slit. A medium resolution soller slit (5°) will expose a length, L , of about 0.5 mm to a given crystallite. Thus, the number of crystallites in diffraction is

$$\eta = \frac{\text{area on unit sphere corresponding to diffraction range}}{\text{area on unit sphere per particle}}$$

$$= \frac{A_d}{A_p} \tag{13}$$

$$A_d = \frac{FL}{R} = 2.5 \times 10^{-4} \text{ steradians}$$

Ratioing A_d to A_p in Table 7 gives the number of crystallites in a given sample. The number for a $40 \text{ }\mu\text{m}$ sample is a surprising 12; hardly enough for good statistics.

To achieve a specific statistical accuracy in the measured intensity, counting statistics of discrete events is a good guide to the number of counts which must be accumulated. The same description may be applied to the number of crystallites in the sample.

$$\sigma = \sqrt{n}/n \quad (14)$$

Diameter	40 μm	10 μm	1 μm
Area per pole (A_p , steradians)	2.11×10^{-5}	3.29×10^{-7}	6.58×10^{-9}
Angle between poles (α_p , degrees)	0.167	0.0209	0.0007
Crystallites in diffraction	12	760	38000

The standard error, 2.3σ , should be less than 1%, thus, n should be greater than 52900 crystallites. Using this number as a guide, even the 1 μm sample fails to meet the desired condition.

This analysis is for a fixed sample with a single diffraction vector per crystallite. Actually, many aspects of the experiment modify the number of effective crystallites in the sample. One of the factors is the diffraction multiplicity due to the crystal symmetry. Because d_{hkl} always equals d_{-h-k-l} for all crystals, there are always two equivalent directions per crystallite. For crystals other than triclinic, the multiplicity may be considerably higher--up to 48 for some cubic reflections. If a variable divergence slit is used, the irradiated area is more than 2 cm^2 . For low absorbing materials, the depth of penetration is increased. A broader range of crystallite divergence, α_s , may be obtained by using the coarser soller slits and a broad-focus diffraction source.

Spinning the sample in the sample plane considerably improves the particle statistics. In Figure 5a, crystallites in position 1 may not be positioned to diffract; but as the sample is spun to position 2, the crystallite finds a position where it does diffract. Bragg planes whose tilt is within the divergence angle may find some position in which diffraction will occur. The axial divergence will also affect the range of crystallite tilt which will allow diffraction. Analyzing the effect of spinning is not simply counting all the grains within a specific orientational range as shown in Figure 6. Crystallite B in position 1 may also diffract in position 2 whereas crystallite A will not diffract in either

position. A crystallite on the spin axis still requires the Bragg planes to be parallel to the sample surface. Spinning usually does bring more crystallites into the irradiated area because the rectangular shape of the irradiated area covers a circular area with spinning. It is evident from this analysis that sample spinning has less effect than is usually assumed. A device for rocking the sample about the diffractometer axis even a few degrees during spinning would bring many more crystallites into diffraction orientation.

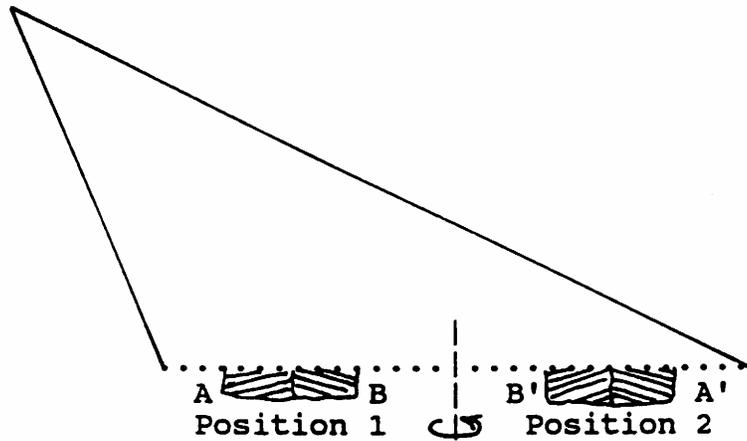


Figure 6. Effect of sample spinning on crystallite diffraction.

Several factors reduce the number of available crystallites or alter the distribution of the diffraction vector. Preferred orientation seriously affects the distribution to the situation where the number of crystallites is not representative of the amount of the phase in any direction and the quantification fails. A wider range of diffraction tilt will improve the measurements; but if the orientation is severe, even a full rotation about the diffractometer axis may not achieve randomness unless the sample is also spinning. Defocusing of the diffracted beam results from sample tilting. This defocusing may be accommodated by using a wider focal slit.

The amount of phase in the mixture reduces the number of crystallites proportional to the volume fraction. Thus, even for a 1 μm sample, phases in concentrations below 10% may have insufficient crystallites for the analytical accuracy desired. Usually, accuracies are quoted in percent absolute rather than percent relative because of the effect of reduced concentration. Determining quartz in a sample at the 0.1% level to an accuracy of $\pm 1\%$ is probably impossible. Comparative studies on the potential accuracy usually suggest $\pm 2\%$ absolute as the limit of modern instrumentation.

Factors such as microabsorption and surface roughness affect the quality of the data measured but do not affect the particle statistics. The absorption, however, significantly affects the depth of penetration of the X-ray beam and hence the effective volume of the sample. Low-absorbing compounds such as organic materials increase the number of available crystallites. High absorbing materials usually present serious problems by reducing the number of available crystallites orders of magnitude.

Particle Size effects and Amorphous Surface Layers

It has been recognized by many researchers following Nagelschmidt *et al.* (1952) and Dempster and Ritchie (1952) that there is a strong effect of particle size on the intensity response of quartz. The general interpretation is that quartz particles develop an X-ray amorphous layer on the surface, and as the particles become smaller, the volume of the amorphous fraction becomes a larger fraction of the total particle volume. Only the crystalline volume contributes to the diffracted peaks, so the intensity response versus weight of sample becomes proportionately smaller.

Early studies by Clelland *et al.* (1952) and Clelland and Ritchie (1952) considered this surface layer highly soluble which would react with various reagents not normally known to affect crystalline quartz. The layer affects the interpretation of silica quantified by chemical methods. Jephcott and Wall (1955), Gordon and Harris (1956), Brindley and Udagawa (1959), Leroux *et al.* (1973) and Atree-Williams *et al.* (1981b) showed how the surface layer also affected X-ray intensity measurements. The layer is estimated to be 0.03 μm thick, and for particles 2 μm or less in diameter, the diffracted intensity is appreciably diminished. This loss in intensity is not to be confused with extinction effects which are stronger in the larger particles. Gordon and Harris showed that the amorphous layer could be removed by acid treatment. Brindley and Udagawa showed that crushed quartz which may develop considerable mechanical damage was susceptible to the formation of the amorphous surface layer suggesting the presence of induced defects as well as ageing initiated vitrification. Edmonds *et al.* (1977) showed how critical was the effect of matching the particle size distribution of the calibration material and the analyte. There is a significant loss of diffraction response per unit weight of quartz when the particle size gets smaller than 2 μm . In a more recent evaluation of the NIOSH Method 7500, Palassis and Jones (19__) have validated the need to modify NIST SRM-1878 by sieving to eliminate the particles > 10 μm . All the problems of particle effects are reviewed by Cline and Snyder (1983, 1985).

Several recent studies have been concerned with this amorphous layer. Nakamura *et al.* (1989) used careful calibration with mixtures of quartz and amorphous silica for calibration and direct analysis and standard addition to quantify the amorphous content of natural quartz samples. The intensity of the amorphous band attributed to the amorphous form was used to quantify the amorphous component. The paper also shows that there is a significant difference in the diffraction pattern of silica glass and silica gel. This result is not surprising because silica gel contains considerable water, and glass is anhydrous. No comparison was made to the opal diffraction patterns. O'Connor and Chang (1986) and Jordan *et al.* (1990) used the Rietveld method to examine many quartz samples also. Their results were similar. All quartz samples have some amorphous component.

STANDARD PROCEDURES

The purpose of this section is to consider the principle steps of the active standard analytical procedures emphasizing the function rather than the mechanics of the procedure. Each procedure will be examined; then they will be compared. Bulk sample treatment will be considered first. There are no certified procedures for bulk analysis of crystalline silica minerals, but there are many usable general procedures described in the literature.

The Analysis of Bulk Samples

The analysis of bulk samples for crystalline silica phases is essentially an extension of the usual quantitative procedures reported in the literature. There is no certified procedure established by any of the federal agencies because the samples to be analyzed have considerable variability in the associated phases, although a very elaborate procedure for analyzing soils which include quartz has been presented by Raab (1988). The NIOSH filter method has been used to analyze bulk materials, but it is not really suitable for the low concentrations as required by OSHA (0.1% quartz) (Blount, 1989) because the sample is not large enough to allow the detection and quantification of this amount. It should also be remembered that crystallite statistics strongly favor the bulk sample because of the larger number of crystallites in the sample.

An excellent review of quantitative procedures has been presented by Snyder and Bish (1989) and a thesis by Cline (1986). The references in these articles cover most of the available literature, and the paper discusses all the main techniques in use today. As mentioned above, there are essentially three methods which are in use: the absorption correction method, the internal standard method and the external standard method. There are also three ways to acquire and process the data in each method. Where applicable, individual peaks may be integrated for each phase, Alexander and Klug (1948). If individual peaks are not resolvable, then clusters of peaks may be used and the contribution of each phase to each cluster may be treated as a matrix, Copeland and Bragg (1958), Karlak and Burnett (1966), Chung (1974a and b, 1975), and Smith, *et al.* (1984). If the overlap is severe, the whole-pattern methods may be used, Wiles and Young (1981), Smith *et al.* (1987, 1988a and b), Hill and Howard (1987), Bish and Howard (1988), Madsen and Hill (1988), O'Connor and Rowan (1988) and Taylor (1991).

There are several methods mentioned in the literature that specifically involve the determination of quartz in bulk samples. The first description is by Clark and Reynolds (1936), and Klug *et al.* (1948) first apply modern theory to silica analysis. The reviews by McGlynn (1968) and Anderson (1975) cover much of the earlier literature. More recent studies will be indicated here. The analysis of quartz and other minerals in rocks is discussed by Pawloski (1985) and Bayliss (1986). Both use the external reference-intensity method. Fluence *et al.* (1969) analyze raw materials and ceramics. Waersted (1986) has used the RIR method to determine quartz in calcium sulfate preparations.

Kamarchik (1980) describes the determination of quartz, talc and clay in paints using the RIR method with TiO₂ as the reference material. Davis *et al.* (1986) has analyzed coal samples using the RIR method coupled with absorption measurements to allow for the fact that not all the phases are determined and the coal component is amorphous. Emig and Smith (1989) have quantified quartz in agricultural dolostone using direct calibration methods because of the minimal interference from the other minerals in the rock. Corrections were required when mica was present. Carter *et al.* (1987) have quantified both quartz and cristobalite in bentonite products using an internal standard method with absorption corrections to allow for the presence of other phases. McKee *et al.* (19__) and Hamilton and Peletis (1991) determined quartz in perlite using spiking with quartz to prepare the calibration curves.

Whole pattern analysis has also been used for some quartz analyses, and as this technique becomes better known, it will be employed more frequently. Smith *et al.* (1989) used whole pattern fitting to analyze quartz and other minerals in sedimentary rocks. Jordan *et al.* (1990) applied the Rietveld method to analyzing quartz specimens for the crystalline fraction. This study applies specifically to the question of the presence of amorphous silica in quartz samples.

It is evident that there are many procedures which could be developed for the determination of quartz in bulk samples. An extension of the above techniques is to employ additional external information as constraints on the X-ray analysis. Renault (1987), Goehner (1982) and Garbaskas and Goehner (1982) and Smith *et al.* (1989) have used chemistry as a constraint on the reduction of the X-ray data. This addition leads to better reconciliation of the physical and chemical data which often causes doubts on the validity of the X-ray results when the two do not agree.

Quartz Analyses using Membrane Filters

NIOSH Method 7500, OSHA/SLC ID-142 July 1989 This method is designed to quantify quartz and cristobalite collected on membrane filters by air samplers or aerosol chambers. It is primarily used for monitoring crystalline silica in atmospheric dust but has been applied to bulk samples as well. Specific collecting conditions and apparatus are specified for the atmospheric samplers. The particles are collected on 37 mm diameter polyvinylchloride, PVC, membrane filters which are then transferred to the analytical laboratory. The PVC filters are then dissolved in tetrahydrofuran, THF, to release the particles which are then transferred to a 25 mm silver membrane filter. This step concentrates the particles to a smaller area and distributes them as an evenly-spaced particle layer for the X-ray diffractometer. This filter and its load are then transferred to the diffractometer for measurement. The desired amount of sample is 2 mg or less. The basis for this analysis have been discussed by Dollberg *et al.* (1980) and Abell *et al.* (1981a).

The X-ray measurement involves the integration of specific peaks for quartz, cristobalite and silver. The process may be run in automated mode (Abell *et al.*, 1978) both to collect the data from each sample following specific steps and interrogate the

information for deciding how to continue with the sample. This program will also process many samples in sequence. The silver peak is scanned to determine the intensity attenuation compared to a clean filter. The attenuation effect allows the thickness of the sample layer to be calculated, and if the thickness is acceptable, at least three peaks for quartz (and/or cristobalite) are scanned. The strongest peak from quartz is measured first to set the count time for all the peaks.

The integrated intensities are converted to weights of quartz or cristobalite using calibration curves from prepared filters with weighed amounts of silica deposited. Standard samples are interspersed with the analytical samples to monitor instrument drift. The weight fractions are determined from the total weight of the sample determined from pre- and post-weighings of the filter during preparation. The detection limits are reported to be 5 µg quartz and 10 µg (*) cristobalite for qualitative determinations and 10 µg quartz and 30 µg (*) cristobalite for quantitative determinations.

* These values reported in the original reference are in error. It is not clear which value is wrong, but the detection limit seems high.

Bulk samples are analyzed by crushing to pass 325 mesh and then taking an aliquot for further processing. When the size range is right, the material is transferred to the silver filter in the same manner as for the calibration procedures. It is now treated in the standard fashion.

HSE Method MDHS 5 1/2, March 1988 This method is reported only for the determination of quartz in airborne dusts, but the principles could apply to the determination of cristobalite with appropriate changes. The method uses the 25 mm diameter PVC or PVC-acrylonitrile copolymer filter in the collection device which is transferred directly to the X-ray diffractometer. Sampling conditions are prescribed. The amount of sample is determined by pre- and post-weighings of the filter. Dust loadings should be kept below 2 mg to prevent loss of dust from the surface of the filter cake during handling and to keep the intensity response versus weight of quartz in the linear range. If the sample is too large, or if there are interfering phases present, an absorption correction may be necessary according to equation 1. The four principle peaks of quartz are monitored depending on the interfering phases which are present as determined by a fast diffractometer scan.

Calibration is performed by preparing standard samples in an aerosol chamber by creating a cloud of airborne quartz dust with an air jet then letting the large particles settle. Four samplers are attached to the cloud chamber. The suspended particles are then drawn through the samplers for prescribed times. The amount of quartz deposited is determined by weight. Progressively longer sampling times create a series of calibration samples. These samples are then measured in the same way that the analytical samples are to be measured. The diffractometer system is monitored by a drift sample such as aluminum.

Dow Chemical Company This method (Henslee and Guerra, 1977) uses PVC filters both to collect the sample and to support it in the X-ray diffractometer. A 25 mm diameter orifice (Gebhardt, 1975) is used in the sampler to restrict the effective part of the filter, and the effective 25 mm circle is cut from the 37 mm filter and mounted on a circular holder that fits the diffractometer spinner. This approach eliminates the need to transfer the sample.

Calibration samples are prepared by crushing quartz to pass a 400 mesh sieve and then settling the particles in ethanol to separate the larger particles and create a sample with a mean size of 5 μ m. A weighed amount of this sample was dispersed in water and then diluted to a fixed concentration. Aliquots of this suspension were then diluted further to specific concentrations and the suspension then filtered through a PVC filter. The actual amount deposited was determined by pre- and post-deposition weights. The intensity calibration curve was linear over the range 0 - 100 μ g/ml. Addition of 20% iron oxides did not affect the magnitude or linearity of the intensity response per unit weight of quartz showing that the iron oxide did not mask the quartz.

U. S. Bureau of Mines, IR-1021, 1975 This method (Freedman, 1972; Thatcher, 1975) collects the dust on 37 mm PVC filters and then transfers the particles to silver membranes by a procedure very close to the NIOSH method. A 1.5% solution of parlodion in amyl acetate may be used to cement heavy dust deposits to the silver filter. The attenuation of the silver peak is used to determine the sample absorption and correct the intensity measurement.

NIOSH Method 7501 for Amorphous Silica As mentioned above, the determination of the amorphous content of a sample is not possible without special processing. Method 7501 uses the property that most amorphous forms of silica will convert to cristobalite with heat treatment. The X-ray analysis steps are similar to Method 7500, but the sample is ashed and fired to 1100 or 1500°C depending on the type of amorphous silica suspected prior to final transfer to the silver filter. The sample is then analyzed for cristobalite. The method depends on the quantitative conversion of the amorphous form to cristobalite without reacting with anything else in the sample.

Other Reported Methods There are several other reports of the use of filter methods for the quantification of quartz. Most of these methods describe the use of the filter method for bulk analysis or analysis where sufficient dust is available for direct processing. Some allow the addition of an internal standard by co-dispersing the phases before depositing on the filter. The methods include reports by Murray and Merkl (19__), Malik and Viswanathan (19__), Clayton Environmental Consultants (19__), Bumsted et al. (19__), and Davis and Johnson (1982a and b). Other methods are reported in papers by Schliephake (1963), Schmelzer (1951, 1955), Plowman (1978), O'Connor and Joklevic (1981) and Kudo (1982).

Several authors have been specifically interested in the determination of cristobalite. The NIOSH Method 7500 does include cristobalite in the procedure and most of the other filter methods could be easily modified to include cristobalite. Kupka

(1967), and Stefanov (1972) describe methods to quantify cristobalite in rocks. Carter *et al.* (1980) quantifies cristobalite in bentonite clays. Janko *et al.* (1989) determine the cristobalite content of dusts in a ceramic plant where it occurs in mullite products and in the atmospheres in the plant.

The determination of cristobalite is not as straightforward as the determination of quartz because its structure is more variable than quartz. The true structure is based on a large unit cell which is a supercell of the simple cubic arrangement usually used to describe cristobalite. The structure lends itself to several types of disorder including distortions which create small domains and stacking faults which lead to some tridymite character. The effect of these defects is to cause the peaks to broaden and shift and change in intensity. Usually the intensity change of the principal peak (101) is less affected than the weak peaks, so quantification is little affected when the peak is integrated by the usual techniques.

Comparisons of Filter Methods

Selection of the Filter Material There is considerable controversy concerning the most appropriate filter for collecting and supporting the dust samples. The organic filters allow the recovery of the particles where the procedure calls for the reconcentration of the particles because the filter is soluble in tetrahydrofuran or other solvent. Where the filters are large, 37 mm, the particles usually require processing to redistribute the particles over a smaller area for effective coverage by the X-ray beam. PVC, polyvinylchloride; PVCA, polyvinylchloride acrylonitrile; Nucleopore polycarbonate, PC; and MCE, mixed cellulose ester have been used for filters. These filters may also be used for direct analysis. MCE filters has the advantage in the X-ray beam of being of low absorption and low scattered background, thus allowing weak diffracted peaks from low particle loadings to be detected. The silver filters and the MCE filters are reported to produce a lower background in the diffraction pattern than the PVC filters. Evaluations of filters have been done by Mark (1974), Henslee and Guerra (1977), Atree-Williams *et al.* (1977), Chung (1978), Dobрева *et al.* (1982), Davis and Johnson (1982a and b), Foster and Walker (1984) and Knight (1984).

The silver filters are used both for collection when the sample is to be analyzed directly and as the substrate when the particles are transferred from an organic filter. One advantage of the silver filters is that they hold the particles better than the organic filters because of their structure, but particles are drawn into the interior of the filter where they are masked from the X-ray beam by the surrounding silver. Thus, a correction factor must be applied for this masking. Another advantage is the crystallinity of the silver which allows the intensity of its diffraction peak to be monitored. If the sample is thicker than one particle layer, the attenuation of the silver intensity provides the sample absorption coefficient. Where the PVC or MCE filters are used for direct analysis, they can be placed over a crystalline support like a silver, aluminum or zinc sample holder to provide the diffracted beam needed to measure the sample attenuation. Greases may be used to hold the filters in place, but the grease may contribute to the diffraction pattern and to the attenuation of the substrate peak intensity.

Direct-on-Filter Methods versus Transfer Methods Several laboratories have preferred to use direct-on-filter methods because of the convenience of simple processing, more rapid analysis and a concomitant improvement in the costs involved. The standard NIOSH Method 7500 is very time consuming, but it is considered to be the accepted legal technique, so all other methods must be compared with it. A very recent evaluation of the direct-on-filter methods was performed by Lorberau et al. (19__). The results of this evaluation showed that the agreement between the NIOSH Method 7500 and the MCE filter method agreed well, but that there was a slight bias in the comparison of the NIOSH method and the silver filter. This bias was thought to be due to a mismatch in particle size between the samples tested, but it might also be due to masking by the silver in the filter.

One of the main drawbacks of the use of direct-on-filter analysis is that the original distribution of particles is spread over the full 37 mm diameter filter. This fact is the primary reason for the concentration step incorporated in the transfer methods. Bradley (1967), Leroux and Powers (1969a and b), Crosby and Hamer (1971), Knight *et al.* (1971, 1972), Leroux *et al.* (1972, 1973), Knight (1975, 1986), Altree-Williams *et al.* (1977), Frevel and Roth (1982) and Kohyama (1985) used direct deposition on silver filters. Gebhardt (1975) modified the personnel samplers to concentrate the particles in the center of the filter by using a aperture with a 25 mm diameter. Others have used this same modification. Chung (1978) and Henslee and Guerra (1977) have examined by direct imaging the distribution of particles collected on filters and showed that personnel samplers do lead to uniform dispersions if run for sufficient time and if the atmosphere is not changing. There is some question whether liquid suspension filtration used to prepare calibration standards yields as uniform a deposit as do the personnel samplers. Spinning the sample during diffraction helps even out the irregularities which do occur. In theory, the particles should be most likely to attach to the filter where the flow rate is the most active, i.e. where no other particles are blocking the passages. This effect should tend to give a uniform distribution of particles as the loading increases.

Calibration

All the methods of quantitative analysis require calibration standards and calibration procedures and tests. For the on-filter methods the particle sizes as well as the minerals must correspond to the samples under study. Obtaining such samples is not easy.

Procedures Because the on-filter methods do not usually use internal or external standards, the standard approach for calibration is to prepare filters loaded with known amounts of silica and establish calibration graphs of intensity response of the specific diffractometer versus weight of silica. The silica should be deposited on the filters in essentially the same manner as for the analyte samples. Elaborate aerosol chambers have been designed for creating uniform deposits by Davis and Johnson (1982b), Davis (1986) and Carsey (1987). Most of the standard procedures prescribe the methods to follow for making the reference standards.

Basically the technique is to disperse the calibrant in a suspension with either air or water and then dilute the suspension to the desired level. The diluted aliquot is then forced through the filter either by vacuum or by pressure. Weighing the filter before and after deposition confirms the loading. The main purpose of the selected procedure is to produce a deposit which is uniform and crystallographically random. Fortunately, the silica minerals show little tendency to orient except on very smooth filters (Edmonds *et al.* 1977).

For bulk samples, the preparation of calibration samples is usually the problem of thoroughly mixing a weighed set of ingredients. Both dry mixing and wet mixing may be used. Individual components should be ground to the desired particle size prior to mixing because size reduction in a mixture usually leads to unsatisfactory results. Except for purity, the materials to be used for the calibrations are probably not as critical as for the filter standards, especially the particle size distribution.

Quartz Very high purity quartz is easily obtained in highly perfect crystals. The question is whether this source is proper for use as a quantitative reference material. The difficulty is that the perfection of the crystallites even after crushing leads to significant extinction effects. Where the quartz in the analyte is natural and coarse grained, this reference is probably acceptable if the crystallite size is equivalent. However, if the quartz is a recrystallization product like chert or produced by reaction, the crystallites may be strained and imperfect altering the intensity response. Simply crushing coarse quartz will not produce the same effect. Thus, the selection of the proper quartz is not always simple. Kacsmar and Tomb (1984) have reviewed suggested materials for quartz calibration.

For respirable quartz, the problem of a suitable quartz is even more acute. Many studies have shown that the particle size distribution affects the intensity response. It is probably more important that the size range be similar to the analyte size range than the precise distribution. There is only one certified quartz standard available for respirable particle analysis. It is distributed by the Office of Standard Reference Data, OSRD, of the National Institutes for Standards and Technology, NIST, as SRM-1878. It has a range of 0.33 to 5.0 μm with an average size of 1.62 μm . It is certified as to purity at >95% quartz. The NIST SRM's are very expensive because of the effort required to certify them. The NIST/OSRD programs for certifying standards have been described by Hubbard (1982) and Dragoo (1986). Chung (1982) suggests Min-U-Sil (Pennsylvania Glass Sand Corp.) as a source of quartz. Currently, 1991, Min-U-Sil is produced in large quantities at many different places and is no longer sufficiently uniform to be an off-the-shelf standard.

Cristobalite OSRD also supplies a cristobalite as SRM-1879 certified as >98.0% crystalline. Chung (1982) reports that cristobalite can also be made in the laboratory by starting with a silica gel or Min-U-Sil and firing it in a platinum crucible at 1450°C for up to 48 hours. The product is usually >99% converted to cristobalite. Diffraction

patterns of cristobalite made in this manner usually show some crystallite size broadening indicating that the average crystallite size is less than 0.2 μm .

Tridymite There is no certified sample available for tridymite. Chung (1982) reports that tridymite may be made by fusing Min-U-Sil in NaCl at 1100°C for 72 hours and then washing the product in water to remove the NaCl. This tridymite must contain substituted Na to stabilize it, but it is suitable as an X-ray standard.

DISCUSSION

Evaluation of QXRPD as a Tool for Crystalline Silica Analysis

Compared with the alternative techniques for analyzing crystalline silica in bulk and respirable samples, XRD is unique in its sensitivity to the specific crystalline phase or phases that may be present in the sample. For identification applications to detect quartz and cristobalite and to determine the interfering minerals, diffraction techniques are fast and easy to apply. For quantification applications, diffraction methods have proved as accurate as any of the other methods available.

Recent comparisons with infrared by Pickard (1985) indicates that the performances of both methods in terms of detection limits and precision is equivalent and acceptable for occupational hygiene surveys at the present exposure limits. Anderson (1975) came to the conclusion that the X-ray diffraction method was unacceptable because there were too many interferences. Other comparisons by Swallow (1978, 1980) and Groff (1980) (quoted in Chung, 1982) using round-robin tests on samples prepared by one laboratory and analyzed by 61 other labs indicate precisions that are generally unacceptable for all methods. Huggens *et al.* (1985) describe another interagency test. No one method stands out as superior to any other method. Precisions, $\text{\AA}/x$ in %, are reported from 28 to 50 % for respirable quartz and 22 to 24 % for cristobalite in a bulk sample. These figures echo earlier reports by Freedman *et al.* (1974), Peters (1976) and Nagelschmidt (1956). Chung (1982) summarizes the situation as follows: "[XRD] needs validated procedures to attain precision; it needs certified primary standards to achieve accuracy." NIOSH Method 7500 is now a validated procedure, and NIST SRM's 1878 and 1879 are certified primary standards. However, this procedure and these standards are for only one specific analysis, that is for the determination of respirable crystalline silica collected in a specific manner.

The objection to the NIOSH Method 7500 is its time-consuming preparation which precludes fast and economic analyses. Many laboratories have proposed and tested alternate procedures which are more economical and which compare favorably to Method 7500. It is apparent that further efforts are needed to locate a more generally acceptable method. Until then, Method 7500 is the only method with any legal significance. The precision and accuracy limits are related to the crystallite statistics discussed below. It may be that the methods are already at the limit.

Specific Problems in QXRPD Analysis

Regardless of the relative accuracy of the XRD methods, its sensitivity to the specific silica phase requires its use in many situations. This section will consider some of the experimental problems that have been recognized in recent years.

Problems Specific to Filter Techniques The many studies involving membrane filters as the collecting and sample supporting method have identified several problems. Different filters have different efficiencies at collecting and retaining particles (Mark, 1974). The organic filters, PVC and MCE, have one side which is smooth and one side which is rougher. The rough side retains particles better, but the smaller particles may be drawn into the interior of the filter and partially masked from the X-ray beam during the analysis. The smooth side is reported to lead to more reproducible results when used for calibration mounts (Edmonds *et al.* 1977). Because of the heavy element, chlorine, the PVC filters have a significant background. MCE filters have considerably lower backgrounds. Silver filters have low backgrounds because of their crystalline nature, but they also exhibit masking effects. The great advantage of silver is that it produces a diffraction peak that does not interfere with quartz or cristobalite. The attenuation of this peak can be used to measure the absorption coefficient of the sample.

Some preferred orientation of quartz has been reported by Edmonds *et al.* (1977). Quartz does have a tendency to fracture subparallel to (101) and may have a cleavage parallel to (100) (Fron del, 1962). The presence of flat surfaces on crushed grains would tend to orient the particles where the substrate is very smooth. This effect is more prominent with large particles, > 15 μm , and with freshly crushed quartz than with small particles and precipitated quartz. The effect is strongest with small amounts of quartz on a smooth filter.

The particle size distribution has proved to be very critical because of the amorphous layer on the quartz particles. Lorberau *et al.* (1991) have illustrated the need to match the size distribution in the calibrating material and the analyte. Even the SRM 1878 needs to be sieved to remove the >10 μm particles. For samples prepared by dispersing small amounts of respirable-sized calibrant as a thin film on a filter and then determining both the sample weight and the intensity response, a significant fraction of amorphous component will strongly diminish the intensity response and alter the calibration curve.

Problems with Bulk Samples The problems of processing bulk samples containing quartz is essentially the same as processing bulk samples in general, and there are many discussions of the difficulties encountered. The two major problems are preparing a sample that is representative of the bulk material and eliminating preferred orientation of the particles if they have a tendency to orient. The first is common to all analytical procedures. An aliquot must be obtained that is equal in composition to the material being analyzed whether it is a bin of raw materials or a small block of a product. This aliquot must then be pulverized to < 5 μm particle sizes and split into smaller

aliquot for the diffraction analysis. The preparation must not allow any particle separation because of different physical properties of the different phases.

Eliminating orientation may be more difficult. There are several suggestions in the literature. Smith and Barrett (1979), Jenkins *et al.* (1986) and Bish and Reynolds (1989) have reviewed sample preparation for diffraction applications in general. Calvert *et al.* (1982) have compared several methods of orientation reduction, some simple, some complex. The side-rifted method of loading sample holders is shown to be the simplest effective method that works well in many cases. In severe cases spheroidizing will be necessary. Smith *et al.* (1979a and b) describe the spheroidizing process in detail which is patterned after a ceramic process called "spray drying". The concept is to create clusters of particles in a spherical shape and then to pack the spheres randomly into a cavity mount. This technique is effective regardless of the shape of the individual particles.

The potential accuracy obtainable from a bulk sample is related to the effective number of particles in the X-ray beam. As seen in the section on crystallite statistics, the number of particles is controlled by the absorption coefficient. The discussion considered a pure quartz sample, but if the quartz is mixed with iron oxide, the effective number of particles is considerably reduced, and the accuracy is also affected. Under ideal conditions using modern diffractometers with high resolution, the maximum achievable accuracy is around 2% absolute.

Detection limits which are usually quoted are for conditions which are ideal, i.e. when there are no interferences for the strongest peak of quartz or cristobalite. Fortunately, this situation does exist for many analyses. Unfortunately, the most common contaminants such as mica and the clay minerals do interfere with the (101) quartz peak and degrade the detection limit significantly as well as affect the quantification accuracy for most analyses. It is difficult to determine a detection limit where interferences exist.

The amorphous surface phase on quartz particles is probably of little significance in most bulk samples. The main reason is that it is really difficult to reduce the particle size to the range where the surface layer becomes dominant. Also, freshly broken particles may not develop the layer immediately, and the diffraction experiment may be completed before the layer forms.

Comments on Standardized Procedures for Respirable Silica

The standard NIOSH Method 7500 is the current legally accepted procedure for determining respirable quartz and cristobalite, and all other methods which are used must be compared with this method. What is the ultimate accuracy of the method? One of the factors in setting the limit of accuracy is the crystal statistics. The analysis for the bulk sample showed that the effective volume of the sample is around 20 mm³. For a respirable dust sample of 2 mg distributed evenly over a filter, the effective volume of sample is 0.75 mm³. This volume is only 4% of the bulk volume, and the crystallite statistics are affected accordingly. Assuming a 2 μm average particle size, the number of effective particles in the sample is 1.8 x 10⁸ and the number in diffraction is around 4000. At the 2.3σ level, the accuracy is around 4% for this number of particles. This figure is an absolute accuracy regardless of the percentage of quartz in the sample. As the percentage of quartz decreases, the relative accuracy increases significantly.

With this estimate of absolute accuracy, it is apparent that the X-ray diffraction method is already near its limit with the present diffractometers. Several of the alternative procedures proposed to increase the economics of running many samples agree with accuracies close to this 4% figure. How then can accuracy be improved? The obvious direction is to increase the effective number of crystallites in diffraction. Use of a larger sample leads to problems in particle retention and masking which requires absorption corrections. It should be more effective to increase the range of diffraction to include more crystallites. Most diffractometers are set up and aligned for maximum resolution. If a broad-focus X-ray tube were used with coarse soller slits and focal slits there would be a wider angular range for crystallites to diffract. If the sample is also rocked a few degrees while it is spinning, the angular range would be increased considerably. Because quantitative measurements are based on intensity, the loss in resolution would be inconsequential, and the quantification accuracy could be improved considerably.

Bulk Sample Analysis

Standardized procedures for quantifying crystalline silica in bulk samples do not exist in the sense of having a single recognized and accepted procedure which has legal status. However, many analytical service laboratories have established procedures specific to their local needs depending on the types of samples to be processed. The biggest single problem is the variability of the matrix in which the silica forms occur and the interfering effects of the matrix compounds. If there are no interferences, quantification down to the detection limit is possible by direct peak integration. If interferences are present, then the procedure must be tailored to this interference. Two main approaches may be used, either a correction is applied for the interfering phase or the interfering phase is removed from the sample prior to the diffraction analysis.

Correction procedures for interfering phases are difficult to apply to diffraction data unless a considerable amount of data is acquired. The interfering phase

concentration must be determined by diffraction effects in parts of the diffraction trace that are free of their own interferences and then the contribution of this concentration to the silica peaks must be subtracted to obtain the silica quantification. Propagation of errors in the individual abundances makes this approach undesirable. The use of whole-pattern fitting methods alleviates some of the difficulties of pattern overlap but not all. Profile fitting of specific peaks also shows some promise but cannot resolve peaks that are directly superimposed.

Pre-concentration methods applied to eliminate the non-silica phases in a sample shows considerable promise. Physical separations are not effective, but chemical methods are. Quartz is sufficiently inert for many phases to be removed in its presence by chemical methods. In fact, the chemical methods for silica analysis rely on the quantitative removal of non-silica phases. For diffraction analysis, only the interfering phases need to be removed, and if 90% of the bulk sample can be eliminated, the silica concentration is increased an order of magnitude. The detection of 0.1% silica becomes the detection of 1% silica which considerably simplifies the analysis. If the silica phase is indeed inert, the concentration factor is simply the weight ratio of the bulk sample pre- and post-treatment. No determination of phases in the matrix is required. Because the samples are bulk with an adequate quantity of material available for an infinitely thick sample, any of the three methods: absorption correction, internal standard or external standard may be employed.

There is considerable doubt that a "standard procedure" for bulk analysis is feasible or desirable. Because of the variability of the matrixes, no single procedure is applicable to all situations. Because no single procedure is feasible, the establishment of any procedure as a "standard" could present legal difficulties in those situations where the "standard" procedure is not appropriate as it might preclude the acceptance of a more accurate appropriate procedure. Whenever legal status of an analysis is required, it would be more suitable to establish a set of criteria for creating and measuring calibration samples and for simulating tests of comparable bulk samples than to define and approve a single "standard" analytical procedure.

The Cristobalite Problem

The quantification of cristobalite requires considerably more study before quantification can be done with confidence. Studies must determine the applicability of diffraction techniques to all situations where cristobalite is encountered in both respirable dust and in bulk samples. It is already established that cristobalite may vary from the well-crystallized form encountered when the temperature of formation is high (~1500°C) to very poorly crystalline forms when the formation temperature is low (~50°C). There are many physical differences which may occur that alter the diffraction pattern, either affecting the shape of the diffraction peak or its angular position. The crystal structure of cristobalite is actually very complex, and there are several polymorphs which may occur. Usually only the low temperature form is encountered, but slight trace of an alkali element may stabilize one of the high-temperature forms. The structure transitions on cooling may lead to considerable twinning and domain structures which decrease the

effective crystallite size. Low temperature growth may lead to very small coherent domains also. Structural defects mostly stacking faults lead to considerable tridymite character. This latter phenomena is common in the devitrification of opal.

Several approaches are available for the quantification of cristobalite. If the full range of the characteristic diffraction peaks are included in the integration, the area which is determined is theoretically proportional to the amount of cristobalite present. However, the possibility of amorphous surface layers as in quartz is very real, and the effect of stacking faults and twinning needs to be evaluated. One possibility exists that may be universally applicable. Heating the sample to 1500°C does convert even the most poorly crystalline silica to well-crystallized cristobalite, so a heat treatment may result in a phase consistent enough for quantification. As long as there is no reaction with other matrix phases, the conversion should be quantitative.

In bulk samples which are the result of firing processes where cristobalite is one of the products, the physical state of the cristobalite may prevent any special treatments. If the cristobalite crystallites are incorporated in ceramic products at grain boundaries or within the other grains, the cristobalite cannot be isolated for additional treatments. Fortunately, the cristobalite is usually well crystallized, but it might be in very tiny crystallite sizes producing peak broadening. X-ray diffraction will detect this cristobalite where other methods may not be as sensitive to it. It would be difficult to establish calibration samples for this situation.

A serious interference problem in the determination of cristobalite is due to the similarity of the diffraction patterns of opal-C, opal-C and cristobalite as illustrated in Figure 3. Even the peak position of the amorphous band in opal-A occurs at the same diffraction angle. Consequently, whenever there is the potential for both phases to be present in the sample being monitored, cristobalite will be overestimated when using any of the standard methods based on the integration of the characteristic peaks. Distinguishing the two phases is not easy, but shape of the diffraction peak is indicative. Where the peak width at half height is larger than usual for the diffractometer in use, opal should be suspected. All opal is paracrystalline, and the diffraction peaks, if any, always show broadening due to the effective crystallite size. Very little cristobalite should show crystallite-size broadening effects in the diffraction pattern. Thus, whenever peak broadening is encountered in the diffraction analysis, it should be reported, and the phase should probably be interpreted as opal. An analysis for water in the sample would support the opal designation. Profile-fitting or pattern-fitting methods of diffraction analysis will help resolve this problem.

The Importance of Tridymite and Other Silicas

There is little to no evidence that tridymite is a significant phase in industrial environments. Based on the SiO₂ phase diagram, it is logical to worry that tridymite might be present in silica products, but the evidence is that tridymite is difficult to form and may not be a stable phase without the presence of an alkali metal to stabilize it. Regardless, there is little justification at this time to spend any effort establishing procedures for its quantification.

The same may be said for the other forms of silica. Coesite and stishovite are so rare in nature that it is a challenge just to concentrate enough to detect in a X-ray pattern. The other crystalline forms would have to be a product of a reaction. Where the material is being produced for manufacture, e.g. a clathrasil, then the material should be monitored. Otherwise, there is no need to set up a general procedure for its quantification. Opal on the other hand, may be a more serious problem that is under estimated. It may be abundant in some environments without recognition, as its amorphous character makes it difficult to detect. More studies should be made on opal, both on how to detect it and on its potential toxicity.

The technique reported for quantifying opal, NIOSH Method 7501, is a viable approach to the detection and quantification of amorphous silicas. The procedure is based on the same method of sample treatment as is recommended for preparing standard samples of cristobalite from a silica precursor (Chung, 1978). Firing at 1500°C quantitatively converts any silica form to cristobalite, even fine-grained quartz. Unfortunately, clay particles and other dust components could react with the silica to form compounds other than cristobalite and reduce the amount of cristobalite formed. The conversion steps including ashing the filter and firing in a platinum crucible may prevent reactions by keeping the particles separated. The major problem is quantitative recovery and transfer of the particles to a substrate for the diffraction analysis.

The Need for Standard Silica Samples

In order to achieve accuracy in any analytical procedure, proper calibration standards are required. At present, 1991, there are only two certified standards available, both supplied by the NIST/OSRD as quartz, SRM-1878, and cristobalite, SRM-1879. The certification for both is phase and chemical composition and average particle size. Atree-Williams et al. (1981a) have described the preparation of quartz standards. Chung (1982) has suggested Min-U-Sil as a standard for quartz and preparation procedures for cristobalite and tridymite. Min-U-Sil is now available from many manufacturers and varies considerably from batch to batch. Before it could be used, a large quantity of a single sample would have to be set aside, homogenized and characterized. A cristobalite prepared by the Chung method is available from The Gem Dugout, State College, PA. Unfortunately, none of these materials are technically certified. Obviously, a program should be initiated somewhere to provide additional certified standards. Unfortunately, the expense of certification is high, adding significantly to the cost of the

material. Only a few laboratories would have the legal status for the certification to be acceptable in court.

Proper certification involves careful physical measurements on aliquots of a sample of sufficient size to provide reference material for many years of supply. The sample should be examined for phase composition, chemical purity, particle size and size distribution, effective crystallite size and crystallite perfection, uniformity of the large mass of material for each parameter, long term stability of the sample, and the feasibility of supplying small aliquots to users at a reasonable cost. For a project such as certification, the cost must be amortized through the sales of the certified samples. Unfortunately, the high cost of each aliquot prevents many users from purchasing the samples and forces the unit cost to be set even higher. It is a "Catch 22" situation.

Samples of cristobalite are much more difficult to obtain than samples of quartz because there is no commercial product available nor is it common in nature. There is a small layered deposit in Eastern Oregon which is 96% SiO₂ and only shows a cristobalite-like pattern by diffraction; however, the percent cristobalite (or opal) has not been determined. This natural material could be homogenized and characterized as a reference sample. Alternatively, a large batch of synthetic cristobalite could be prepared by a method similar to that described by Chung (1982) then homogenized and characterized. The high temperature of the synthesis, > 1500°C, precludes its routine synthesis in readily available laboratory furnaces. Also, because it needs to be fired in a platinum container, only small batches may be processed at any one time. There are ways to fire larger batches at temperatures up to 1600°C, but they would require special arrangements with ceramic processors and might "contaminate" a production line with silica.

Tridymite would have to be synthesized because there is no adequate natural source. First, it would have to be established that tridymite was indeed required. Its synthesis temperature, 1100°C, is a more reasonable laboratory temperature, but it would still have to be prepared in small batches.

It is feasible for individual laboratories to synthesize small batches, but not to carry out the full characterization. Although the properties would be reasonably consistent to other batches synthesized in the same manner, such a product would not have the legal status of a certified standard. Particle size could vary considerably depending on how the material was treated after recovery from the crucible. Proper crushing could be tailored to provide specific size and size distributions.

Calibration Curves and Correction Factors

The most common procedure for calibrating the intensity response for the filter methods is to prepare a series of filters with uniformly deposited, weighed amounts of the crystalline silica phase. The intensity response is then measured and plotted versus weight of silica on the filter. As long as the response is linear, there is no particle interference, and no correction is necessary unless masking occurs in a highly absorbing

filter such as silver. A departure from linearity usually implies particle masking which then requires an absorption correction. However, theoretical absorption corrections assume a continuous thin layer of sample which is not appropriate to thin particle dispersions which are discontinuous layers. Applying a correction for the absorption effect is difficult with discontinuous samples until the samples are many layers thick to average out the individual particle variations. Thus, it is wise to avoid samples with more than 2 mg on a filter which is where the particles tend to overlap significantly. However, where the absorption is measured directly on the analysis sample by transmission, the averaging effect of the X-ray beam compensates somewhat for the discontinuous distribution. In spite of the inherent difficulties, Casciani and Ripanucci (1984) do report nomograms for the determination of quartz content where the intensity response is not linear.

For bulk samples, absorption corrections are appropriate, but they are more difficult to measure. Because of the thickness of the samples, transmission methods on the same sample are impossible, and a second preparation must be made for the attenuation measurement. Most diffractionists prefer to avoid the absorption correction and to employ either the internal-standard or external-standard method which are feasible for bulk samples.

Detection Limits

The minimum detection limit, MDL, of crystalline silica in very small samples is as important as its quantification at any level. Most health regulations define a personal exposure level, PEL, or a maximum concentration above which action must be taken. What is critical is that the MDL of the analytical procedure be well below the PEL.

Tolerance limits are quoted in $\text{mg}\cdot\text{m}^{-3}$ for atmospheres and weight percent for bulk samples. X-ray diffraction measures weight of a sample on a filter or weight percent of a bulk sample. The weight measurement must be converted to weight per unit volume by correcting for the amount of air sampled. Typical samplers filter $1.7 \text{ l}\cdot\text{min}^{-1}$ which amounts to about 800 l in an 8 hour working shift. Thus, for respirable silica at the PEL, the amount would be 25 μg of quartz. Most procedures are reporting MDL values of 3 - 5 μg which is within the PEL. If the total mass of the sample is 2 mg, the MDL is below 1% with an accuracy around 4%.

For bulk samples the MDL is reported to be around 0.03 weight percent (Emig and Smith, 1989) without interferences using present equipment. Another report by Schreiner (1990) claims a detection limit of 0.01%. This value is insufficient to assure the PTL of 0.1 weight percent for bulk products because the accuracy of 2% is outside the acceptance range. Bulk samples may also be treated as respirable samples by depositing on a filter substrate, but Blount (1989) has shown that the MDL is insufficient to be meaningful.

RECOMMENDATIONS

The modern diffractometer is aligned for optimum resolution. Recommended changes to the diffractometer to increase the particle statistics will improve the accuracy and detection limits for both on-filter methods and bulk samples.

Modifications to the Diffractometer for Quantification

Accurate intensity information on samples being processed for quantification are degraded by a diffractometer aligned for high resolution because too few crystallites in the sample are allowed to diffract. Longer counting times will not improve the statistics unless other changes are made. The situation may be considerably improved by making changes to the diffractometer which are suggested by the analysis of crystallite statistics. First, a broad-focus X-ray tube should be employed, and the focal slit should be enlarged. Second, the soller slit should be replaced by the coarsest slit available or eliminated entirely. Third, a divergence slit should be used which allows the incident beam to cover the entire sample surface at the angle of measurement. Finally, an attachment should be constructed which will simultaneously rock the sample on the diffractometer axis while the sample is spinning. The rocking angle should be plus and minus one to two degrees. Care must be taken that the spinning and rocking motions are not synchronized, so that full coverage of the increased diffraction range is assured. The defocusing due to the rocking and the use of the broad-focus source will be covered by the larger focal slit. Longer counting times will now improve the intensity measurements by allowing time for the angular coverage of the sample by the rocking and spinning motions.

Because the limiting aspect of the diffraction pattern for the quantification of the small amounts required in silica analysis is the peak-to-background ratio, it is necessary to improve this ratio by all means possible. The above recommendations address increasing the peak intensities. Equivalent efforts should be focussed toward decreasing the background level of the diffraction pattern. Two procedures should be incorporated in all measurements. Scattering from the atmosphere surrounding the sample should be eliminated by using a helium path for the X-ray beam. All sample holders should be designed to contribute no undesirable diffraction scattering to the experiment. This latter condition may be accomplished by constructing the sample support from a single crystal oriented not to cause any diffraction. Glass or other amorphous materials are unsatisfactory for this purpose. Ironically, single-crystal quartz is an excellent material for this function.

An additional modification to the diffractometer would be to employ a position sensitive detector rather than the conventional detector. Because resolution is not required, the PSD would cover a broader range of angles without requiring the diffractometer to be scanned during the sample rocking and spinning. If the diffractometer is used entirely for quantitative analysis, the suggested changes could be permanent. Only the interchange of the X-ray tubes, which requires realignment, is a time-consuming change or a change which incapacitates the diffractometer from serving as a multipurpose instrument.

Modifications to Sampling

The main goal of preparing a sample for X-ray quantification is to optimize the crystallite statistics. However, in the case of personnel samplers, the sample is limited to the number of particles accumulated during a working shift. Ideally, this value could be zero, then no problems would exist. The small size of the collected samples does provide a challenge to preparing the most effective sample. The goal is now to take full advantage of the sample area intercepted by the incident X-ray beam in the diffractometer with the particles that were collected. In the modern diffractometer with fixed or variable slits, the effective area is around 2.5 cm². Spinning the sample increases the area to around 3.2 cm². The particles should be spread uniformly over this area. A 2 mg sample with an average particle size of 2.5 μm will just fill this area with a single layer of densely packed grains. It is evident that 2 mg of sample is the limit for effective use of thin-layer techniques unless the area is enlarged.

The main improvement to respirable dust measurements would be to increase the usable area in the diffractometer, so the full 37 mm filter could be used. The increase in size of the sample area would cause some defocusing of the diffracted X-ray beam, but the low resolution geometry already recommended allows for this defocusing. It is suggested that the use of the direct on-filter approach could be significantly improved by employing larger filters than the 25 mm size used in the currently recommended techniques providing longer sampling times or higher flow rates would add more particles to fully cover the filter. The improved crystallite statistics would probably provide better comparisons between the on-filter methods and the transfer methods and would certainly improve the comparisons between the X-ray diffraction methods and other methods such as infrared.

Other Recommendations

More calibration standards are needed for both quartz and cristobalite. These standards should be well characterized for particle size and size distributions as well as for effects such as extinction and the presence of the amorphous surface layers. Tridymite is not a significant industrial phase and probably does not need to be quantified. Opal and other amorphous silicas, on the other hand, probably do need to be quantified, and appropriate standards are needed.

The present NIOSH Method 7500 is a good method for quantification and has legal status, but it is time-consuming and not economical for large numbers of analyses. Direct on-filter methods are adequate for personnel monitoring purposes on a routine basis, and a direct method should be certified.

More studies are necessary on the quantification of cristobalite in respirable samples and in bulk samples. If the toxicity is indeed more than for quartz, the frequency of cristobalite in the workplace requires a better knowledge of its abundance in industrial atmospheres and dusts.

Quantification of opal and other amorphous silicas also requires more study. The techniques involving conversion of the amorphous forms to crystalline cristobalite show considerable promise, but interfering reactions and quantification of the conversion need to be evaluated.

SUMMARY

X-ray diffraction techniques are appropriate for the identification and quantification of crystalline silica phases. In fact, they are the only positive way to identify which of the crystalline phases is present in environmental samples. At present the accuracy of quantification in respirable samples is around 4 % absolute and 1 % for bulk samples. This accuracy may be improved with a few modifications to the diffraction equipment used to collect the data. Detectability limits are around 3 μ g for respirable quartz on filter substrates and 0.03 weight percent in bulk samples where there are no interferences.

The methods for bulk samples may be improved significantly by preconcentrating the silica phases with chemical treatments prior to the diffraction measurements. Eliminating 90 % of the matrix in a bulk sample increases the silica level by an order of magnitude, and the 0.1 weight percent would then be 1 %. Even in the presence of interfering phases, modern diffractometry with digitized intensity information and new mathematical approaches to decomposing overlapped diffraction peaks will provide the necessary intensity values for phase quantification.

Certifying a single standard procedure for bulk analysis by X-ray diffraction is unwise and probably impossible. The types of samples and differences in matrixes are too varied to allow a single method to be employed. Although the matrix does not affect the diffraction from the silica phase per se, it does partially mask the phase by contributing to the absorption effect of the sample. Also, some diffraction peaks may interfere with the silica peaks in some cases. It is far more appropriate to develop a set of calibrated samples and criteria for certifying each individual procedure established by independent laboratories for specific sample types. The certification should require prescribed reproducibility and accuracy on test samples of comparable composition to the samples for which the procedure is intended.

Quantification is very sensitive to sample preparation methods primarily because of the tendency of the particles to orient crystallographically when packed in a sample. The small size of the respirable silica grains and the lack of a cleavage or other orienting influence minimizes this problem. Even in bulk samples whose grain size is small, this problem is minimal for the silica minerals. The bigger problem in bulk samples is often reducing the particle size small enough to satisfy particle statistics.

Matrix effects are not a problem in the thin samples used for respirable samples. In bulk samples, the matrix effects, which are primarily due to differential absorption effects, do not affect the diffraction patterns but do affect the intensity

response. Intensity effects may be corrected for by absorption measurements or the use of internal or external standards. The matrix has no effect on the detection limits in respirable samples provided there are no peak interferences, but highly absorbing phases can mask the silica in bulk samples. When the particle sizes are larger than respirable, microabsorption also becomes a problem.

Particle size is also a problem when an amorphous layer forms on the surface of the silica particles which is well documented for quartz. As the size of the particles becomes smaller, the volume of this surface layer becomes significant, and the diffraction intensity response departs from linearity with respect to the amount of silica present. The most critical effect is when the particle size distribution of the analytes does not match the material used for calibration.

There are two certified standards produced by OSRD/NIST which are useful for calibration of respirable silica, but the particle size distribution does not always match the desired distribution of the samples under study. No certified standards are available for bulk calibration, and it will probably be difficult to create any because of the variability of samples to be analyzed. Several standard methods have been established by federal agencies for respirable silica. The NIOSH transfer method needs to be further evaluated to simplify the sample preparation, because the present method is not economic for the large number of samples that need analyzing. Individual companies and analytical service laboratories have set up and tested procedures for bulk analyses for specific types of samples. Although none of the methods are generally applicable, all the techniques are based on one of the three general methods of powder diffraction analysis: absorption measurement, internal or external standard.

Modern diffraction instrumentation is adequate for the measurements to be performed. Computerized instruments allow the data to be digitized for easy mathematical processing. Data collection parameters are flexible and usually defined by the amount of silica in the sample. Longer count times are needed for smaller amounts to maintain the statistical significance of the measurements. Step size and scan range are less important except when there are peak interferences which require more of the diffraction pattern to be measured. The instrumental measurements are not the time or cost limiting aspect of the use of diffraction methods; it is the sample preparation time that controls the numbers of samples that can be processed and the economics of making large numbers of measurements.

Several studies are warranted to improve the current status of diffraction analysis for the quantification of crystalline silica. Additional standards need to be certified in sufficient quantities to supply needs for many years. Both quartz and cristobalite are necessary. Some certified bulk samples should also be prepared, and a series of round-robin tests should be performed to test the individual methods in use in different industrial laboratories. Such a set of samples could be used to certify new laboratories. The use of modern mathematical methods of profile fitting and pattern matching for data analysis need to be evaluated for determining the intensities of the diffraction peaks compared to the usual methods of peak integration. The recommendations on

defocussing the diffractometer to improve crystallite statistics need to be tested to determine how much improvement can be accomplished by the changes suggested.

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APPENDIX

Computer Programs for Peak Analysis and Quantification

This information is taken from Smith and Gorter (1991). For addresses of authors, readers are directed to this reference.

Table A1: CODES USED IN THE PROGRAM LISTS
PROGRAM LANGUAGE

A	ASSEMBLY	GWB	GW Basic
Alg	ALGOL	P	PASCAL
B	BASIC	QB	QUICK BASIC
C	C	TB	TURBO BASIC
F	FORTRAN IV, 77, ANSI	TC	TURBO C
GFA	ATARI	TP	TURBO PASCAL

COMPUTER TYPE

MF	Main Frames:	CDC, Cray, IBM, PDP, VAX
PC	Personal Computer:	IBM, MAC
TS	Time-Sharing	
O	Other Types	ENCORE, FACOM, PRIME

DISTRIBUTION FORM OF PROGRAM CODES

S	Source Code
E	Execution Codes Only
EK	Key Required to Run
EP	Execution Codes Only with Permission of Philips Netherlands

COSTS AND CONDITIONS FOR DISTRIBUTION OF CODES

C	Commercial Product
F	Free
L	Lease and Fee
\$	Small Fee <\$100
\$\$	Large Fee >\$100
FL	Free for noncommercial users, Lease and Fee for commercial users

TYPE OF DOCUMENTATION

DF	Machine-Readable Documentation
M	Manual
N	No documentation
R	Reference

PROGRAMS SUPPORT

A	Author support
N	No support
blank	No indication

PROGRAM SOURCES

PEB	Program is available from the Powder Diffraction Software Exchange Bank of the Dutch Association of Crystallographers.
*	Source address or reference not available
OLD	An old program available from many sources

Table A2 PROFILE FITTING - DECOMPOSITION

<u>Program</u>	<u>Lang.</u>	<u>Computer</u>		<u>Form</u>	<u>Cost</u>	<u>Supp.</u>	<u>Doc.</u>	<u>Source</u>
		<u>MF</u>	<u>PC</u>					
ABFfit	F,P	+	+	E	\$\$	A	M	Antoniadis et al.
AUTOPEAK	F	+	-	S	F	A	DF	RAL
CUVFIT		+	-					Wang et al.
DIFFRACT-T/FIT	F,A	-	+	E	C	A	M	SOCABIM
DOREES	F,P	+	-	E	\$\$	A	DF	Jansen
FIT	TC	-	+	E	F	A	R	Petkov-Bakaltchev/PEB
KET, KETA	F	-	+	E	\$\$	A	M	Vladimiz
LAT1	F	+	-	S	F	A	R	Tran
LSQPROF	F,P	+	-	E	\$\$	A	DF	Jansen
MicroSHADOW	F	-	+	EK	C	A	M	QJohnson
PEAK	F	+	+	E	\$\$	A	M	GUFI
Pi'oPiliPa'a	F	+	-	S	F	A	M	Jones
POWDER								Rossel/Scott
POWDERPATTERN	F	+	-	S	F		R	Hubbard/Pyrros
PROFAN	F	+	-	S	\$	A	R	Will et al.
PROFAN/PC	TP	-	+	S	F	A	R	Merz et al.
PROFIT	F	+	+	S	\$\$	A	M	Sonneveld/Langford
PRO-FIT	F	+	-	S	F	A	R	Toraya/PEB
REGION	F	+	-	S				Hubbard/Pyrros
SCRAP	F	+	-					Cooper
SHADOW	F	+	-	S	F	A	DF	SHoward/PEB
TOFMANY	F	+	-	S	F	A	DF	IPNS
TXTPVGT	TP	-	+	S	\$	A	DF	Bourniquel et al.
XRAYL	F	+	-	S	F	A		Zhang/ Hubbard

Table A3 PROFILE FITTING - FULL PATTERN

<u>Program</u>	<u>Lang.</u>	<u>Computer</u>		<u>Form</u>	<u>Cost</u>	<u>Supp.</u>	<u>Doc.</u>	<u>Source</u>
		<u>MF</u>	<u>PC</u>					
ALLHKL	F	+	-	S	F	A	DF	Pawley
EDINP	F	+	-	E	\$	A	R	Pawley
FINAX	F	+	-	S	\$	A	R	Hovestreydt
FULLPROF	F	+	+	E	F	A	DF	Rodriguez-Carvajal
POWLS	F	+	+	S	\$\$	A	M	Will
PROFIT	F	-	+	S	F	N	M	Scott
WPPF	F	+	-	S	F	A	DF	Toraya

With the availability of accurate digitized diffraction traces, peak analysis is becoming a very popular option for locating peaks and for determining the profile parameters. The terminology of profile analysis is confusing for diffractionists who are starting this type of analysis. The programs in this section are correctly classified as decomposition programs. Each of these programs uses a predetermined profile either defined analytically or "learned" from an isolated peak to fit all the other peaks in the pattern including the α_2 component. This procedure is to be distinguished from deconvolution which is a Fourier analysis of the peak shape. There are several ways to approach the problem of decomposition.

First, the peaks can all be considered as independent, and each profile can be fit using free parameters. Usually, the profile shape is fixed and the parameters of peak intensity, profile half-width, and peak position are varied. The relative positions of the α_1 and the α_2 components are known, and their intensity ratios are fixed at 0.5. Where there is a mixture of phases, the peak shape may vary among the phases. If crystallite size is a factor and the crystallite shape is non-spherical, the half-width may vary within the peaks of the same phase. It should be apparent from this discussion that no single program can be optimized for all these options.

The programs listed under the heading "Profile Fitting - Decomposition" differ from the ones listed under "Profile Fitting - Full Pattern" in the way the peaks are treated. In the former category, each peak is generally considered as independent of the other peaks even in a cluster, and usually only a limited range of the pattern is considered during each application of the program. In the latter category, all the peaks (or a large number) in the pattern are considered at one time. If the sample is single phase, all the peak positions are related, and the program should constrain the peak locations to those compatible with a unit cell. Usually, the profile shape is also constrained. The purpose of this approach is to resolve individual peaks, so that the intensities can be determined. The single goal of this approach is to obtain intensities for crystal structure analysis. These intensities can then be used with the usual single-crystal analysis programs which employ direct methods and Patterson analysis. All the programs in this section operate on the full pattern to provide individual intensities.

Table A4 QUANTITATIVE ANALYSIS

<u>Program</u>	<u>Lang.</u>	<u>Computer</u>		<u>Form</u>	<u>Cost</u>	<u>Supp.</u>	<u>Doc.</u>	<u>Source</u>
		<u>MF</u>	<u>PC</u>					
ARCOQUANT	F	+	-	S	\$\$	A	DF	DSmith
DBW-4.1	F	+	-	S	F	A	M	Bish/SHoward
DBW3.2S	F	+	-	S	F	A	M	Young
DBW3.2 (Mod. PEB)	F	+	-	S	F	A	M	Wiles-Young/PEB
FAZAN	F,P	-	+	S	\$\$	A	DF	Burova et al.
GMQUANT	F	+	-	S	F	A	DF	DSmith/PEB
HOWARD-2.0	F	+	-	S	F	A	M	SHoward
LSQX	F	+	+		C	A	N	Vonk
MicroQUANT	F	-	+	EK	C	A	M	QJohnson
++PADS++	F	-	+	E	C	A		WASSERMANN
PC/PEAKS	C	-	+	S	C	A	M	Hill/Foxworthy
PC/QXRD	F	-	+	S	\$\$	A	M	Hill
PFLS	F	+	-	S	F	A	R	Toraya
PLUVA	F	+	-		\$\$	A	DF	Schenk
QPDA	F	+	-	E	F	A	M	Hill/Madsen
QUANT85	F	+	-	S	F	A	M	Hubbard/Snyder
RIMPAC	GWB	-	+	E	\$\$	A	M	Davis
SIROQUANT	F	-	+	E	C	A	M	Taylor

Quantitative phase analysis by X-ray powder diffraction is one of the few techniques which is truly phase sensitive rather than element sensitive. The first applications followed the development of the theory by Alexander and Klug (1948). Although the technique was applied effectively to some special problems, the data collection was laborious and limited the general application of the method. When the APD became the data collector, the data was easier to analyze, and the technique saw enhanced use in the 1980's which has continued to the present time.

There are basically three ways of doing quantitative analysis at the present time. One technique uses integrated intensities (areas) of individual peaks for each of the phases in the mixture if peaks are resolvable and clusters of peaks when they are not. With the raw data in digitized form, it is easy to integrate the desired diffraction ranges for the calculation. QUANT85, PC/PEAKS, MicroQUANT and RIMPAC use this approach. GMQUANT and ARCOQUANT use the full diffraction trace with a reference database of digitized traces of reference patterns. The other programs are Rietveld programs modified to emphasize the quantification of phases in a mixture by adjusting the pattern scale factors for absorption effects. All these approaches are effective if the sample preparation problems can be overcome.